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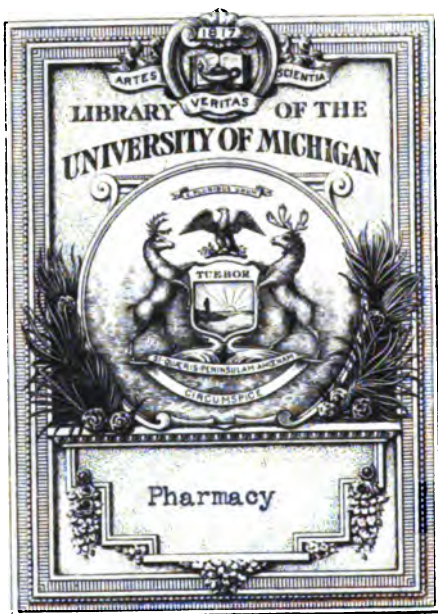
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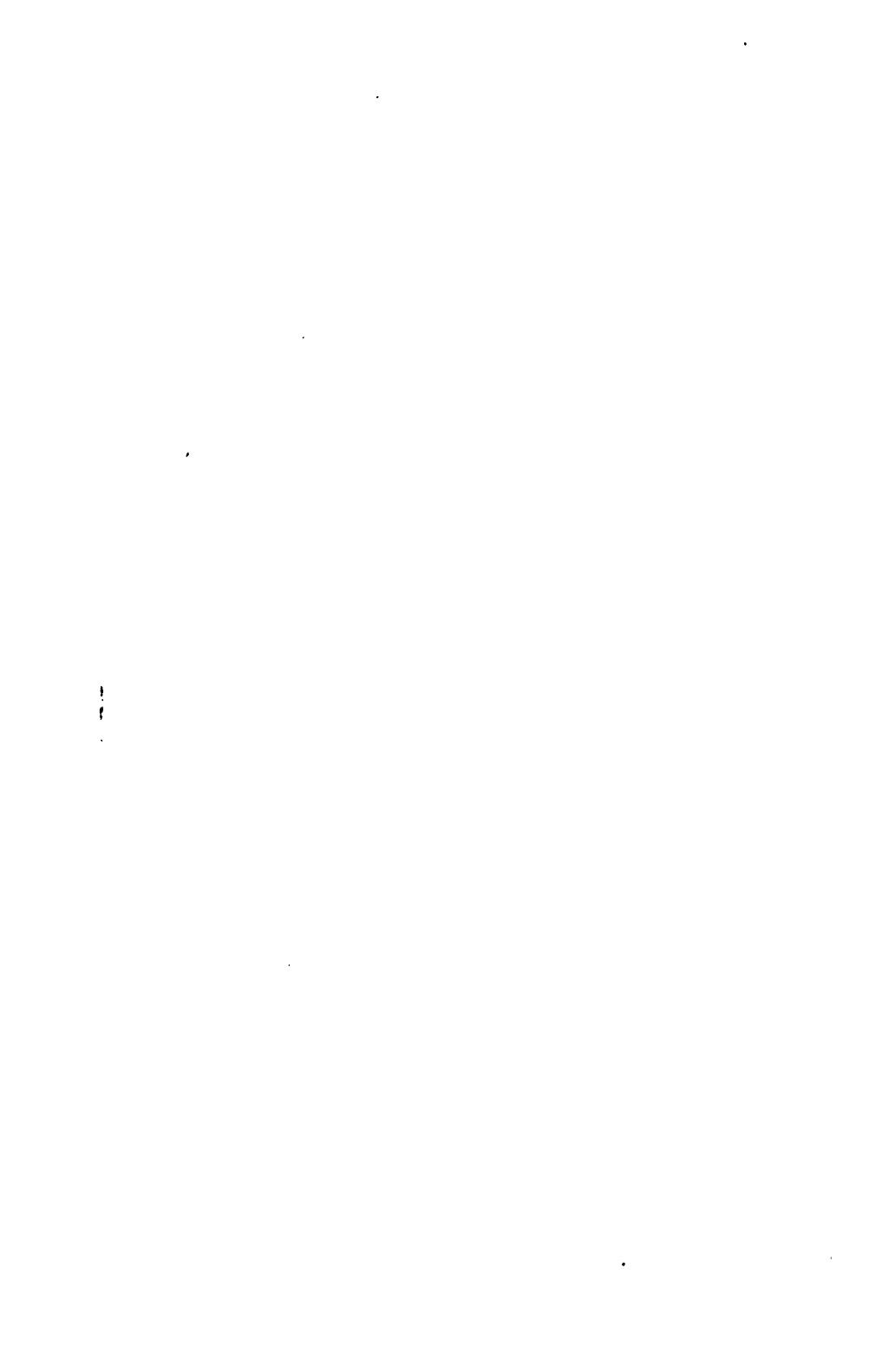
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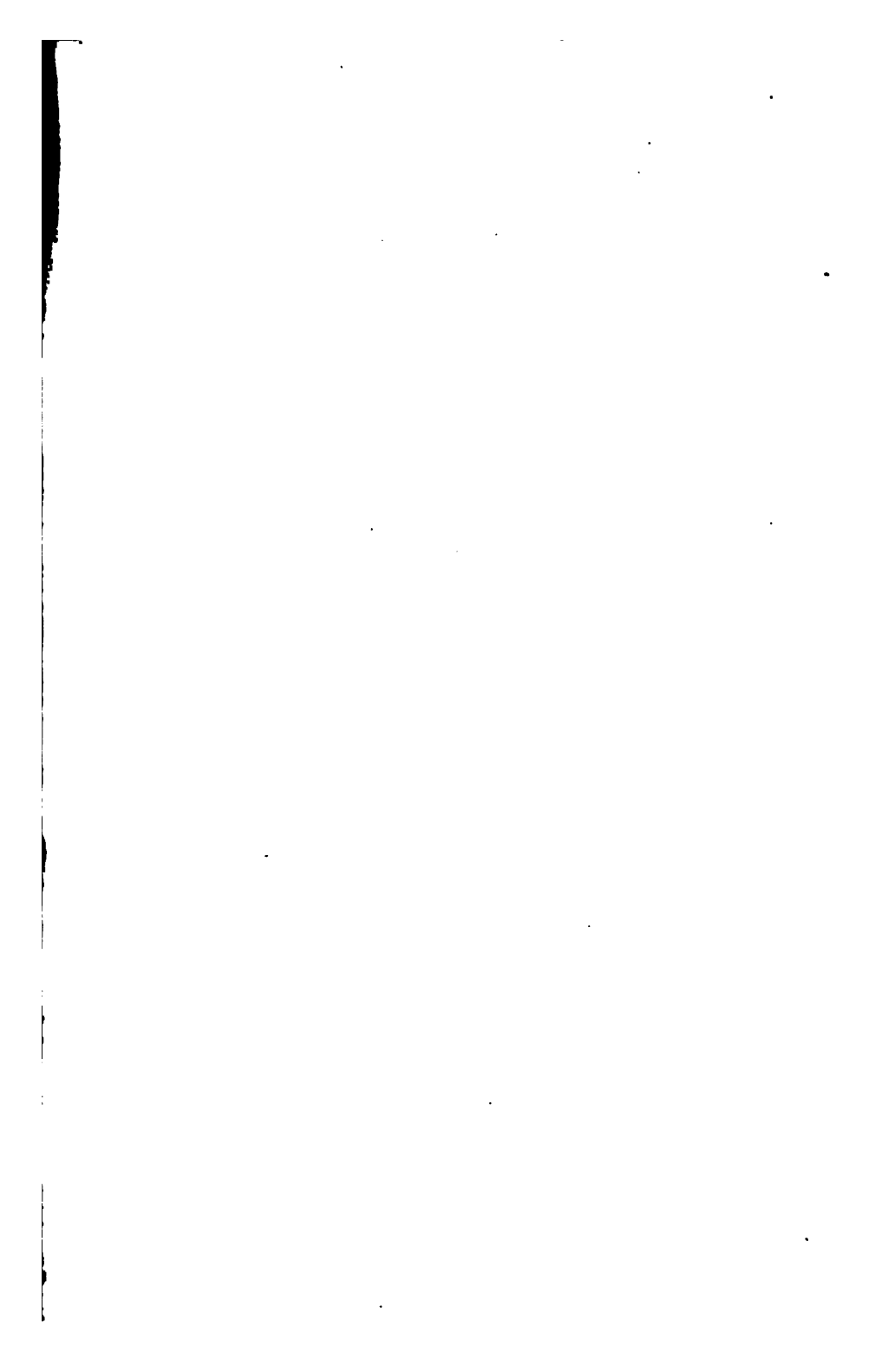
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# INTRODUCTION TO INORGANIC CHEMISTRY

BY  
**ALEXANDER S MITH**

**PROFESSOR OF CHEMISTRY AND ADMINISTRATIVE HEAD OF THE DEPARTMENT  
OF CHEMISTRY IN COLUMBIA UNIVERSITY, NEW YORK**

**Third Edition**

***REWRITTEN***



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## PREFACE TO THE FIRST EDITION

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THIS book, the first draft of which was written six years ago, is the outgrowth of the introductory course in chemistry which the author has given for the past fifteen years. A subject undergoing the persistent, though unconscious criticism of keen minds should gain in self-consistency and coherence as it is presented year after year. For example, an answer must be found for the common question, "Why does the chemistry of the laboratory differ from the chemistry of the text-book and the lecture to such an extent that they seem to be different sciences?" The chemistry of the laboratory is, of course, the only real chemistry, and that of the lecture must be somewhere at fault. The student neither sees nor weighs atoms, for instance, and so the details of the laboratory experiment, which *are* seen and studied, become the basis of the whole treatment. The atom and the ion assume the rôle of merely figurative aids in the description of the facts. Gradually the conception of chemical equilibrium comes to contribute the major part of the explanation which is essential to the evolution of a *system of chemistry* founded upon experiment.

In the choice and arrangement of the material, several principles have served as guides :

The book is intended primarily for students beginning the study of chemistry in a college, university, or professional school. It is assumed that use of the book goes hand in hand with systematically arranged laboratory work in general chemistry. The first four chapters, for example, contain a discussion of a few typical experiments. They appeal directly to experience derived from the performance and observation of these and other similar experiments in the laboratory and in the class-room. In these chapters some of the features which are characteristic of every chemical phenomenon are sought out, put into words, and illustrated.

No conception is defined, and no generalization or law is developed, until such a point has been reached that applications of the conception and experimental illustrations, later to be related in the law, have *already* been encountered, and there is about to be occasion for further applications and illustrations of the same things in the chapters immediately succeeding. In these chapters the applications are frequent and explicit. Later, page references in parentheses continue to indicate the recurrence of examples which might otherwise fail to be noticed. It is one thing to come to *know* a principle of the science, and quite another thing to have acquired, by constant repetition of the process, a confirmed *habit of using* the principle on every appropriate occasion. To assist still further in the attainment of this end, an attempt is made in the last six chapters again to mention and illustrate, by way of review, the most important principles of the science.

No conception or principle is given at all, unless, in its most elementary aspects, it can be made clear to a beginner; and unless it is capable of numerous applications in elementary work; and, finally, unless a knowledge of it is of material use in organizing and unifying the result of such elementary work.

An attempt has been made to state the laws and to define the conceptions of the science in terms of experimental facts. The figurative language of hypothesis has been employed only in explanations.

Familiarity with physical conceptions and facts is so indispensable to the chemist that no apology is needed for the rather full treatment which some of them have received.

No two chemists would agree perfectly in regard to the apportionment of space. The processes of chemical industry, and the every-day applications of chemical science, cannot all be mentioned. These fields, and that of mineralogy, can be represented by examples, without the incompleteness of the result being in any way a detriment to a work of a general character. Again, a dense array of descriptive material, unilluminated by explanation, is a positive injury to an introductory treatise. All reference to historical matters cannot be omitted, but a logical display of the subject can be achieved with comparatively

•

little of the history. Of all the aspects of the science, the theoretical is thus the one whose treatment is susceptible of least abbreviation.

The principles of chemical equilibrium are (and have been for the past half-century) fully as much required for intelligent consideration of the simplest experiment, as is the theory of combining proportions itself. Important parts of the theories of solutions and of the battery are much more recent, but each is equally indispensable to the understanding of matters which cannot long be withheld from the notice of the beginner. Surely space ought not to be saved by entire omission of essential parts of the chief thing that makes chemistry at all worthy of a place amongst the sciences. Nor may we attain brevity, no matter how great the temptation, by condensing the passages on theory until they reach the limit of comprehensibility by an expert. Without clear exposition, full illustration, and frequent application, laws and principles simply repel, or worse still, mislead the beginner.

We reach the same conclusion from another view-point. Every student should have access to, and should use, reference books devoted especially to descriptive, industrial, historical, and physical chemistry, and to mineralogy and crystallography — at least one good book in each of these five subjects. With the help of the index, the veriest tyro can find in a few moments, almost anything he wants in four out of five of these branches. But just the opposite is the case with the theory. Only an expert realizes what information he is in need of, and knows under what titles to look for it. And often even the expert would fail to understand the isolated sentence or paragraph when found. In a large proportion of connections the beginner simply cannot use such a book for rapid reference at all. In many lines, therefore, much may be left to outside reading, but for theory almost no dependence can be placed on reference work in other books.

For the reasons enumerated above, an unusually large proportion of space has been given to theoretical matters. The actual amount of theory is no greater than is usual in books of the same class, but the explanations are often fuller. Even so, the beginner will probably find that some parts form reading as stiff as any he is accustomed to undertake, without complaint, in physics or mathematics. It can only

be said that easily read modes of presenting the science of chemistry are apt to delude the beginner into thinking he has mastered the subject, when in reality he has simply been steered clear of the chief difficulties.

The order of topics was determined by many considerations, jointly. For example, in the first week of his work, a student may encounter experiments, in connection with which, almost every part of chemical theory might usefully be discussed. But mastery of the theory must necessarily come bit by bit, and the theory is therefore distributed through the book. Instead of being introduced as soon as a fragment offers a chance for explanation, the treatment of each of the various theoretical subjects, as far as possible, has been postponed until a whole chapter could be devoted to it. The result makes subsequent reference easier, and facilitates alterations in the order of study. Thus, the hypothesis of ions is not mentioned as soon as it well might be, because satisfactory treatment of it must follow the molecular and atomic hypotheses of which it is an extension, and because the full explanation of this hypothesis must be preceded by some account of the phenomena of electrolysis and of the essential properties of solutions, and, also, by a discussion of chemical equilibrium, a subject which of necessity presupposes two or three months' work in chemistry. There is another disadvantage which arises from a premature explanation of the hypothesis of ionization. When it appears at an early stage, too long an interval separates this subject from the study of the metallic elements, and the details are largely forgotten before the field for their chief employment is reached.

The paragraphs in smaller type are not intended for beginners, but for advanced students and teachers, which accounts for the fact that reference will frequently be found in them to subjects treated systematically in later chapters.

The exercises and problems are simply samples of some of the various kinds of questions which might be raised in dozens at the end of every chapter.

Recent works on general chemistry have been consulted during the revision of the manuscript. Of these A. A. Noyes' admirable *General*

*Principles*, Ostwald's *Grundlinien* — a veritable *tour de force*, and Bloxam's *Chemistry* may be mentioned as having proved most suggestive. The author owes special thanks to several friends who have undertaken the toilsome work of reading part or all of the book in manuscript or in proof, and in particular to his colleagues Messrs. Julius Stieglitz, H. N. McCoy, L. W. Jones, and E. S. Hall, to Dr. J. B. Tingle of Johns Hopkins University, to Mr. C. M. Wirick of the R. T. Crane High School, Chicago, and to Mr. Maurice Pincoffs of Chicago. The author alone is responsible for any defects which may be inherent in the plan of the book and for errors which may have escaped detection, but must gratefully acknowledge the very great benefit the book has derived from the friendly criticism of these gentlemen. Other corrections or suggestions will be gladly received by the author.

CHICAGO, *January*, 1906.

ALEXANDER SMITH.





## PREFACE TO THE THIRD EDITION

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THE general arrangement of the book has not been altered, excepting that the difficult chapter on the oxygen acids of chlorine has been transferred to a later position. The contents have been brought up to date. The introductory chapters have been improved. More applications of chemistry have been introduced. Various methods of writing equations are discussed. Additional paragraphs for advanced students (in small type) dealing with various points of view in regard to subjects like valence, and with the logical arrangement of matters like chemical properties, have been added. Experiments suited for demonstration purposes have been designated by the sign [Lect. exp.].

In order to induce the student to carry the book to and from the laboratory, the volume, as in the previous editions, has been made as compact as possible by the use of narrow margins and specially made, thin paper.

The author is greatly indebted to many friends, whose suggestions have been utilized in the revision. He is also under great obligations to Dr. J. E. Booge, Dr. George Scatchard, and Mr. Kenneth P. Monroe for coöperating in the reading of the proofs, and for the many corrections and improvements to which they have called his attention.

NEW YORK, *January* 1917.

ALEXANDER SMITH.



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**INTRODUCTION TO  
GENERAL INORGANIC CHEMISTRY**



# INTRODUCTION TO INORGANIC CHEMISTRY

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## CHAPTER I

### CHEMICAL PHENOMENA, AND THE METHODS OF STUDYING AND OF CLASSIFYING THEM

HUMAN knowledge has become, in recent times, so extensive and complex that the truths ascertained have had to be divided, more or less arbitrarily, into groups. Thus, the study of animals, their classification by structure, life-history, distribution, and so forth, form the group known as zoölogy. Such a group is called a *science*, and includes a more or less *distinct* body of knowledge. There is a widely spread impression that a *science*, like chemistry, is a part of the natural order of the Universe. It is thought that we are trying to find the boundaries of chemistry, as they have been predetermined by nature, and to discover the facts, relations of facts, and laws which nature has provided as a means of classifying the content of the science. Now, the situation is precisely the reverse of this. Nature provides only the materials and the phenomena, and *man* is attempting to classify them. He divides the whole into groups, such as physics, chemistry, botany, etc. Then he classifies the facts within each group, in order that he may more easily remember them and perceive their relations. He often finds that, when new facts are discovered, parts of the classification have to be changed.

That the boundaries of these groups are purely arbitrary, however, and do not exist in the subject-matter itself, is seen at once in our own treatment of them. Thus, for convenience, we take the structure of animals *by itself* and style it anatomy; but we include in the science of physiology the study of the way in which the parts of *both plants and animals* perform their functions; and we assemble cognate parts of two groups in sciences like astro-physics and physical chemistry. The sciences, therefore, are not mutually exclusive, and their boundaries overlap in every direction.



The difficulty in deciding what are the most convenient boundaries is as great with chemistry as with other groups. At the one extreme we have the **abstract sciences**, logic and mathematics. At the other extreme lie the **concrete sciences** like geology, zoölogy, and astronomy. The former are not concerned primarily with the study of matter at all, but with that of abstract conceptions. The latter deal with definite aggregates of matter, such as the nature and history of a particular deposit of sulphur and their relation to those of other deposits of sulphur, or the structure and history of a particular collection of organic material known as a pike, and their relation to the structure and history of a mass of similar material called a salmon. Between these two sets of sciences are the regions occupied by the **abstract-concrete sciences**, physics and chemistry. These sciences deal in part with the same portions of matter, but in a more abstract way than do geology or biology. To them, all specimens of pure sulphur are alike, whether they have been formed by volcanic action, or have been deposited by bacteria in an entirely different manner. In particular, the line which divides physics and chemistry from one another is often difficult to draw. It is assumed, however, that the reader is already familiar with the elements of physics, and so, in place of entering upon an academic discussion of the nature of this line, we shall allow its location to emerge as we proceed.

The same principle of grouping is pursued *within* each field. Thus the preparation and properties of chemical compounds is called **descriptive chemistry**. The content of this portion of the subject is in turn divided into **organic** chemistry (dealing with almost all the compounds containing carbon) and **inorganic** chemistry, and the content of each of these is further classified according to a plan involving the consideration of the constituents of each compound. The study of the proportions of the constituents in compounds, of the conditions under which chemical action occurs, and related matters of a more abstract character, are grouped together in **theoretical chemistry**, which is likewise subdivided. Again, the means that have been devised for recognizing the components of mixtures or compounds and measuring their quantities constitute the several branches of **analysis**. The subdivisions of chemistry of this kind are numerous, *e.g.*, industrial chemistry, bio-chemistry, food chemistry, radio-active chemistry, and so forth.

The ideal in view in thus classifying the content of a science is to convert it into an **organized body of knowledge**. The various ways used to organize the facts of a science will be presented in detail as

opportunity offers. These ways constitute what is called the **scientific method**.

It is only by following intelligently the way in which the science is manufactured, step by step, out of the raw material furnished by observation and experiment, that the student can gain a sound foundation for more advanced work in the same science, or a mental training broad enough in its tendency to add measurably to his efficiency in every other task. The chief object of useful thought, no matter whether the problem is one of language, history, business, or life, is to organize isolated facts into knowledge, and the means of successfully accomplishing this is the use of the scientific method.

**What Chemistry Deals With.**—Chemistry is the science which deals with *all* forms of matter. It considers the natural kinds, such as rocks and minerals, as well as materials like fat and flour obtained from animals or plants. It deals also with artificial products like paints or explosives. When we wish information about any specimen or kind of matter, we consult a chemist. Now chemists have worked out a point of view which enables them to attack any problem connected with matter in a systematic manner and to state the results in a clear and simple way. **To learn chemistry**, we must **first strive to acquire this point of view and to learn the technical language** the chemist uses in stating and discussing his results.

**Properties.**—Suppose that a piece of rusty iron is submitted to the chemist. He at once examines the rust and notes that it is reddish-brown in color and earthy in appearance. He separates some of it from the iron and finds it to be brittle, that is, easily broken and capable of being pulverized in a mortar. He finds that its density is about 4.5, that is to say, 1 c.c. (Appendix I) of it weighs about 4.5 g. (1 c.c. of water at 4° weighs 1 g.). On heating some of it in a flame, he finds that it does not melt, and must, therefore, have a very high melting-point. These qualities he calls *properties*, and more especially physical properties. Since all specimens of iron-rust show exactly the same properties, he often calls them **specific physical properties**, because they are **properties shown by all specimens of a particular species of matter**.

After removing any rust by filing or scraping, the chemist examines the iron, and finds a fresh, clean surface to be almost white and metallic in appearance. The metal is tenacious, so that it can

be bent but not easily broken. He finds that its density is about 7.5, and that the metal is incapable of being melted in an ordinary flame. In addition, he finds it to be strongly attracted by a magnet, while rust is not attracted.

The chemist, then, studies what he calls the specific physical properties of each material, in order that he may be able to recognize various materials.

**Substances.** — All specimens of iron show one set of properties and all specimens of iron-rust show a different set, peculiar to rust. The chemist calls **any definite variety of matter, all specimens of which show the same properties, a substance.** Iron is one substance and rust another. A substance is recognized by its properties.

That all bodies of a like kind have identical properties is the most fundamental fact in chemistry. This fact is called the **Law of specific physical properties**, and is stated thus: **The specific physical properties of a substance are constant in all specimens.**

The point of view of the chemist consists, therefore, in describing any material by ascertaining whether it is made of one, or of more than one substance. **He describes it by naming the substances which, by a study of their properties, he has found in it.**

The foregoing definition of a substance is very incomplete. Thus, a three per cent solution of common salt in water always has the same properties, yet it is not one substance, but a solution containing several substances. This definition is sufficient for the present purpose, however.

**Two Illustrations of the Study and Description of Materials.** — If a piece of **granite** is examined by a chemist, he observes at once that it is spotted in appearance, and made up of several crystalline materials of differing nature. He therefore breaks it up and studies the *properties* of the fragments. Some of the fragments of granite are dark and with a penknife can easily be split into transparent sheets, thinner than paper. These particular fragments are in all respects like *mica* (Fig. 1). This substance is a mineral which, in certain neighborhoods, occurs in large masses, and sheets of it ("isinglass") are used to close the windows of stoves. Others of the fragments are clear like glass, and are very hard (see Appendix II), and have *all* the properties of *quartz* or rock crystal (Fig. 2), which is another substance well known to the chemist. The remaining fragments are less clear than quartz, and are not so

hard. They can be split into layers, but not nearly so easily as can mica. They form oblong crystals, differing in this also from quartz, which shows hexagonal crystals.\* This substance is *felspar* (Fig. 3). Thus the chemist studies the physical properties of the fragments, and finds that there are three different substances in granite. He reports that the components of granite are mica, quartz, and felspar.



FIG. 1.

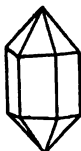


FIG. 2.

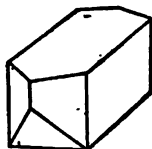


FIG. 3.

When flour is examined by the chemist, it appears to the eye to be all alike. Under the microscope, even, all he can learn is that it consists largely of grains, which have the characteristic appearance (first property) of grains of starch (Fig. 4). He places some flour on a square piece of cheese-cloth and encloses it by tying with a thread (Fig. 5). On kneading the little bag in a vessel of water,



FIG. 4.



FIG. 5.

milky water is squeezed out. When the milky water stands, the white material settles to the bottom, the water can be poured off, and the deposit can be dried. This white substance, when boiled with water, gives an almost clear liquid which jellies on cooling. This is another property of starch. A little tincture of iodine (solu-

\* Crystals (see also Index) are natural forms of geometrical outline, which solid substances assume. Usually each substance has a more or less distinct form of its own, the particular angles at which the faces meet being peculiar to the substance. Its individual crystalline form is therefore a specific physical property of each substance.

tion of iodine in alcohol), dropped on a part of the starch, causes the latter to turn blue. This is a very characteristic property of (and therefore *test* for) starch. When the bag of flour is kneaded persistently in water which is frequently changed, the material finally ceases to render the water milky. The starch has all been washed out. When the bag is now opened, a sticky material is found in it. This is called *gluten*. The chemist therefore finds that the flour contains starch and gluten. He learns this by *separating* the components.

**Law of Component Substances.** — Every material can be described as being composed of one substance, or as being a mixture of two or more component substances, each of which has a definite set of specific physical properties. This is the second fundamental law of chemistry. This conception was first clearly stated by Lomonossov (1742), a Russian author, statesman, and chemist (1711-1765).

**Mixtures and Impurities.** — A material containing more than one component substance is called a *mixture*. The characteristic of a mixture is that each of the component substances, although mixed with the others, possesses exactly the same properties as if it were present alone. No one of the components affects any other component or alters any of its properties. Granite and flour are typical mixtures.

When a specimen is composed mainly of one substance, and contains only minute amounts of one or more other substances, it is frequently spoken of as a specimen of the main substance containing certain specified substances as *impurities*. To be called an impurity, the foreign matter need not be dirty or offensive. Thus, common salt usually contains a little magnesium chloride, a white crystalline solid, as an impurity, and it is this impurity which becomes damp in wet weather. Again, compounds of lime and of magnesium are common impurities in drinking water.

**Chemically pure (C.P.)** means that the quantities of the impurities which the material is most apt to contain have been reduced below the amount which would interfere with the most exact chemical work for which the substance is commonly employed. Absolutely pure bodies are unknown.

By convention we continually speak of "*pure*" hydrochloric acid, or of "*pure*" sulphuric acid, although there may be more than 60 per

cent of water present in the former, and 7 per cent in the latter. By this we mean to distinguish the former from "commercial" hydrochloric acid, for example, which contains, in addition to the water, impurities like sulphuric acid and a coloring matter. The water is in fact disregarded, since it is assumed to be present in all cases.

**Components.** — The ingredients of a mixture are called the **components** (Lat., *componere*, to put together), because they are simply placed together, without change, and can be separated without change.

**Bodies or Specimens.** It will be seen that *substance* is a general term, like the word "dog," covering the whole species. The *substance* iron includes all the iron in the Universe, and all that was made in the past or may be made in the future. When we refer to a particular piece of iron, we call it a **body** or a **specimen**.

A **body** is any particular specimen of matter, such as a piece of sulphur, a portion of water, a piece of ferrous sulphide, a fragment of granite, or some nitrate of silver solution. There are thus as many bodies as there are discrete portions of matter. A body may be heterogeneous, or made up of visibly unlike parts, as granite and a mixture of iron powder and sulphur are; or it may be homogeneous, or alike in all parts, as are pieces of sulphur and of ferrous sulphide and portions of water and of nitrate of silver solution.

**The Rusting of Metals.** — If we return once more to the subject of rusty iron, we find another point which interests the chemist. If the iron is kept moist — for example, by lying in the grass or partly immersed in water — the layer of rust gradually becomes thicker, and the core of iron becomes thinner until it finally disappears. The rust seems to be *formed from the iron*, in presence of air and moisture. The iron, particle by particle, loses the properties of iron and simultaneously acquires those of rust. Now, the chemist is concerned, not only with recognizing substances, but also with the ways in which substances change and new substances are produced.

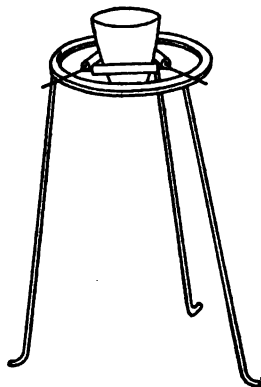


FIG. 6.

Several other metals rust, as does iron, but the change is slower. Thus, lead rusts (tarnishes) slowly, and zinc still more slowly. The change can be hastened by heating. If some lead be melted in a porcelain crucible (Fig. 6) and be stirred with an iron wire, a dirty yellow powder collects on the surface. Gradually more and more of the powder is formed and less and less of the metallic lead remains, until at last all the metal is gone. Melted tin, when treated in the same way, gives a white powder.

**Explanation of Rusting.**—The first fact which seemed to throw light on the subject was discovered by a French physician, Jean Rey (1630), who found that the rusts of tin and lead, made by heating and stirring, were *heavier* than the original pieces of metal. He inferred, correctly, that the additional material which caused the increase in weight came from the air. He imagined, however, that the rust was not a new substance, but a sort of froth, and therefore a mixture of air with the metal. Other investigators, such as Hooke (1635–1703) and particularly Mayow (1645–1679), in England, explained the increase in weight by supposing that some material from the air had *combined with* the metal. In other words, iron, for example, was one substance composed of iron only, and rust was another substance, made by union of iron and a material from the air, and not a mere mixture.

It was Lomonossov (1756) who first proved by an experiment that the extra material did come from the air. He placed some tin in a flask, sealed up the mouth of the vessel, and weighed the whole. The flask was then heated and the tin was converted into the white powder. So long as the flask remained sealed, no change in weight was found to have occurred. When the mouth of the flask was opened, however, some air rushed in, and the total weight was then found to be greater. Evidently a portion of the original air, during the heating, had forsaken the gaseous condition and joined itself to the tin to form the powder. This left a partial vacuum in the flask, and more air entered when the latter was opened. Eighteen years later the same experiment was made by Lavoisier, who drew the same conclusion. The rusting of other metals was found to be due to the same cause. Lavoisier named the gas, taken from the air, oxygen.

The conclusion can be confirmed in various ways. For example, when the air is pumped out of the flask before it is sealed, the metal can be heated in the vacuum indefinitely without rusting.

A rough imitation of the rusting of iron may be shown to be accompanied by an increase in weight. Iron powder is suspended by means of a magnet over one pan of a balance, and the equipoise is restored by placing small shot on the other pan. When the iron is heated, union with oxygen begins and, after a time, the pointer inclines markedly to one side. The product here is magnetic oxide of iron  $\text{Fe}_3\text{O}_4$ , however, and not rust  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ .

**Experiment to Show the Nature of Rusting.** — That a part of the air is consumed when iron rusts is easily proved. We moisten the interior of a test-tube and sprinkle some powdered iron so that it covers and adheres to the whole interior surface. We then set the tube mouth downwards in a dish of water (Fig. 7). At first, the pressure of the water compresses the air in the tube very slightly, and the water ascends above the mouth to the extent of a small fraction of an inch only. As the moist iron slowly rusts, however, the oxygen is gradually removed, and the pressure of the atmosphere outside slowly pushes the water further up the tube. After an hour or more, the water has ascended about one-fifth of the total distance towards the top of the tube. Evidently part of the air has changed from the gaseous condition, and the water has been forced up to take its place. Inspection now shows some reddish particles, where rusting has taken place. The rust, then, contains part of the iron and all the oxygen that the tube contained.

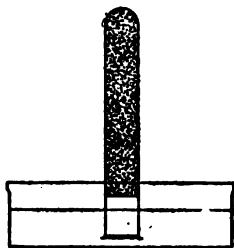


FIG. 7.

Of course, much of the iron powder is still grey, and has not rusted. The air in the tube did not contain oxygen enough to combine with all the iron. The iron that remains is as little able to rust in the remaining gas as in a vacuum.

Incidentally we learn from this experiment that atmospheric air contains about one-fifth (20 per cent) oxygen by volume. The remaining four-fifths is almost all nitrogen (79 per cent), a substance which combines with very few materials, while the balance (1 per cent) is made up of gases which do not enter into combination with any known substance. If lead, tin, or zinc had been heated in an enclosed volume of air, they likewise would have taken out the 20 per cent of oxygen and would have left the other gases.

**An Older View: Phlogiston.** — Simple and satisfactory as this explanation appears to us, it must be said that it gained little sym-



pathy from the contemporaries of Rey, Hooke, and Mayow. The other investigators had been prejudiced by a remarkable hypothesis which was supposed to explain both rusting and combustion. Starting with a suggestion of Plato's, that during combustion some material escaped from the burning body, and that the flames and heat represented the vigor with which this substance rushed out, Stahl and Becher invented the idea that a substance, which they called "phlogiston," was contained in all materials capable of rusting or burning. Its escape accounted for the phenomena of combustion, and its absence for the alteration in properties of the residual substance. They were perfectly aware that the material was heavier after rusting than before, but refused to sacrifice their hypothesis to a mere fact like this. So they ingeniously appended the suggestion that phlogiston was a substance which not only was not subject to gravitation, but possessed the opposite property of levity! Thus, its escape rendered the material from which it issued heavier than before! Instead of demanding the preparation and examination of phlogiston itself, and the demonstration that it weighed less than nothing, the generality of chemists of that age accepted the idea without proof. It is not surprising, therefore, that many of their attempts to explain chemical experiments on the basis of an assumption which was the precise opposite of the truth should have resulted in hopeless confusion. The fact that foreign matter was actually gained by a body during the process of rusting was not generally accepted until it was demonstrated anew by Lavoisier in 1774 (p. 8). The whole development of chemistry was stunted by the general belief in the conception of phlogiston and, during the one hundred and fifty years which passed between the work of Jean Rey and his contemporaries, and that of Lavoisier, relatively little progress was made.

The introduction of the balance into the chemical laboratory, and the first use of measurements of weight as a means of exploring and explaining chemical changes, is frequently ascribed to Lavoisier. As a matter of fact, it is difficult to state when measurement of weight first became the chief ally of the chemist in his work. Important and conclusive results were obtained by its means, however, before the time of Lavoisier, for example, by Jean Rey, Boyle, Lomonossov, and Black (1728-1799).

**Explanation in Science.** — One section (p. 8) was entitled *Explanation of rusting*. If that paragraph be now re-read, it will be found that, in the ordinary (as distinct from the scientific) sense of the word, no explanation was given! When we ask a man to "ex-

plain" some feature in his conduct, we recognize that he might have chosen to act otherwise, and we wish to know *why* he acted precisely as he did. Nature, however, has no free will, and cannot tell why she presents certain phenomena, and not others.

On examining the explanation, we find that it simply shows that, when iron rusts, it combines with oxygen from the air. This is an additional fact. It shows *how* iron rusts, namely by taking up oxygen, but not why it is able to unite with oxygen. We simply do not know why iron can combine with oxygen gas and platinum can not.

Explanations in chemistry are of three kinds. (1) We usually try to show that the phenomenon is not an isolated one. Thus, we show that other metals rust. This reconciles us to some extent to the fact that iron rusts, and we feel some mental satisfaction. This is the method of **showing that the fact to be explained is a member of a large class of similar facts.** (2) Next we try to get **more information about the fact to be explained.** Thus, when, to the acquaintance with the outward manifestations of rusting, we add the further information that there is an increase in weight, and that this is due to union of oxygen from the air with the iron, we feel increased satisfaction, and say that the fact has been "explained." (3) If we are still dissatisfied, and can discover no further useful facts, we **imagine a state of affairs which, if true, would classify the fact or add to what we know about it.** This step we call explaining by means of an **hypothesis.** We then devote our attention to trying to verify the hypothesis. The making of attempts to explain facts is part of the Scientific Method (p. 3).

**The Law of Chemical Change.** — The three examples of rusting show that specimens of matter can lose their original properties and acquire new ones. Since a substance is "a species of matter, with a constant set of properties," we are compelled to decide that, when a material changes its properties, it has, in doing so, become a new substance. This consideration calls to our attention the third of the fundamental laws of chemistry, namely, that **the material forming one or more substances (such as oxygen and iron), without ceasing to exist, may be changed into one or more entirely different substances.** Such a change is called a **chemical change, or action, or interaction, or reaction.**

The commoner kinds of chemical actions can be divided, for convenience, into four varieties. We can now define the first of these.

**First Variety of Chemical Change: Combination.** — In each case of rusting, two substances (a gas and a metal) come together to form a third substance (an earthy powder). Apparently two substances may come together in two different ways. They may form a mixture, in which both substances are present, and retain their properties, or they may come together to form a single substance with different properties. When two (or more) substances unite to form one substance, the change is called **chemical combination** or **union**. The product is called a **compound substance**.

We are very careful never to speak of a compound substance as a mixture. Rust is not a mixture of iron and oxygen; it shows none of the properties of either. Nor do we call a mixture (like granite) a compound, or the operation of mixing, combination or union. These are technical words in chemistry and, to avoid confusion, may be used only with due regard to their technical meanings.

**Constituents.** — As we have seen, we speak of the substances in a mixture as the components. When we wish to refer to the forms of matter which are chemically united in a compound, we call them the **constituents** (Lat., *con* and *statuere*, to stand together) of the compound substance. Thus, iron and oxygen are the constituents of rust.

The chemist **separates** (p. 6) the components of a mixture, for that is all that is necessary. He **liberates** the constituents of a compound, however, because *they* are bound together in chemical combination.

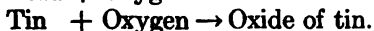
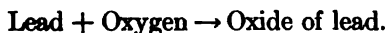
The names given to compounds are usually devised so as to indicate the nature of the constituents. Thus, iron-rust is oxide of iron (or ferric oxide, from Lat. *ferrum*, iron). The yellowish powder from lead is lead oxide or oxide of lead, and the white powder from tin is oxide of tin.

**A Condensed Form of Statement.** — We may represent a chemical combination, or indeed any kind of chemical change, in a condensed form, thus:



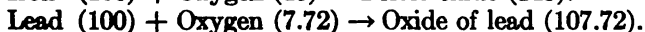
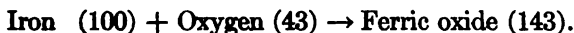
Each name stands for a substance. Two substances in contact with one another (mixed), but not united chemically, are connected by the + sign. The arrow shows where the chemical change comes in, and the direction of the change. We read the statement thus:

Iron and oxygen brought together under suitable conditions undergo chemical change into oxide of iron, called also ferric oxide. Similarly we may write:

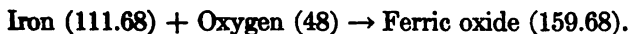


**The Increase in Weight in Rusting.** — As we have seen, the process of rusting is accompanied by a slow increase in the weight of the solid, due to the gradual addition of oxygen to the metal. Now, this increase in weight ceases of its own accord, when a certain maximum has been reached. This occurs when the last particles of the metal have disappeared. Thus, the lead gains in weight until every 100 parts of the metal have gained 7.72 parts of oxygen, and the tin until every 100 parts have gained 26.9 parts of oxygen. When these increases have occurred, the metal is found to have been all used up, and prolonged heating and stirring cause no further absorption of oxygen and no further change in weight. This fact, that each substance limits itself of its own accord to combining with a fixed proportion of the other substance, in forming a given compound, is one of the most striking facts about chemical combination. In mixtures, any proportions chosen by the experimenter may be used. In chemical union, the experimenter has no choice; the proportions are determined by the substances themselves. Thus, 100 parts of iron, when turning into ordinary, red rust, take up 43 parts of oxygen, no more and no less.

This fact enables us to make our condensed statements more specific and complete by including in them the proportions by weight used in the chemical change:



The following numbers, which represent the same proportions by weight, are the ones commonly used by chemists:



**Summary.** — Thus far, we have learned that chemistry deals with substances and their physical properties, and with the changes which substances undergo. We have discussed and defined a number of important words expressing fundamental chemical ideas. Finally, we have touched upon the weights of the materials used in chemical

change, a subject of great importance which will be developed further in a later chapter.

We must now take up four new examples of chemical change. They will aid us in introducing one or two additional conceptions and laws that are continually used by the chemist, and without which we cannot begin the systematic study of the science.

**Another Case of Combination: Iron and Sulphur.** — Since oxygen is an invisible gas, there is a slight difficulty in realizing that rusting consists in the union of *two* substances — this gas and a metal. The present example is less interesting historically, but it is simpler because both substances are visible and are easily handled. The case of iron and sulphur will enable us to illustrate the same point of view and to practice the application of the same technical words. It will also introduce us to two manipulations — filtration and evaporation — which are frequently used by the chemist.

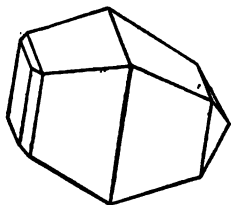


FIG. 8.

We begin by observing the physical properties of the two substances. Those of iron have already been noted (pp. 3-4).<sup>\*</sup> Sulphur is a pale-yellow substance of low density (p. 3), namely, 2. It is easily melted (m.-p. 112.8°). It does not dissolve in water — that is, it does not mix completely with and disappear in water, as sugar does on stirring. It does dissolve readily in carbon disulphide, however (41 parts: 100 at 18°). It crystallizes in rhombic forms (Fig. 8). It is not attracted by a magnet.

**Study of the Mixture, before Combination.** — Now, if some iron filings and pulverized sulphur are stirred together in a mortar, the result is a *mixture*. True, the color is not that of either sub-

<sup>\*</sup> References to previous pages are used in order to save needless repetition in writing. The beginner, however, requires endless repetition in his reading and must form the habit of examining, in conjunction with the current text, the parts referred to. The passages cited are, by the reference, made part of the current text, which will usually not be clear without them. The same remark applies to topics referred to by name. Such topics, if treated in later pages, are distinguished by the letters *q.v.* (*quod vide* = which see), and must be sought in the index.

All terms, and especially those borrowed from physics, if not perfectly familiar, must be looked up in a work on physics or in a dictionary.

stance, but with a lens particles of both substances can be seen. Passing a magnet over the mixture will easily remove a part of the iron, and with the help of a lens and a needle the mixture can be picked apart, particle by particle, completely. We can **separate** the *components* of the mixture more expeditiously, however, by using manipulations based upon certain **suitable properties**. Thus, sulphur dissolves in carbon disulphide while iron does not. If, therefore, a part of the mixture is placed in a dry test-tube along with some carbon disulphide (Fig. 9) and is shaken, the liquid dissolves the sulphur and leaves the iron. To complete the separation, the iron must be removed from the liquid by filtration, and the sulphur recovered by evaporation of the carbon disulphide.

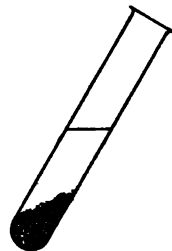


FIG. 9.

**Filtration.** — Iron, or any solid, when mixed with a liquid or solution (like the solution of sulphur in carbon disulphide) is said to be **suspended** in the liquid. If the solid is one that settles rapidly, the liquid may be separated from the solid in a rough way by pouring off as much of the clear liquid as possible. This is called **decantation**.

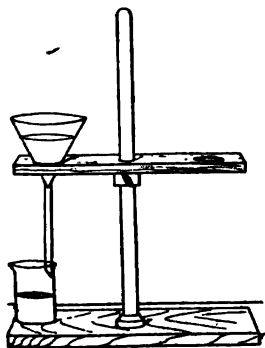


FIG. 10.

A complete separation is best made by pouring the mixture on to a cone of filter paper supported in a glass funnel (Fig. 10). The liquid, together with anything that may be dissolved in it, runs through the pores of the paper and down the hollow stem of the funnel. The liquid is then called the **filtrate**. The particles of the suspended solid are too large to pass through the pores, and so collect on the surface of

the filter paper. This operation, like everything the chemist does, takes advantage of the physical properties of the various materials.

The material remaining on the paper (the **residue**), when dry, is wholly attracted by a magnet and shows all the other properties of iron.

**Evaporation.** — To recover the sulphur, the solution in carbon disulphide — the filtrate — is poured into a porcelain evaporating dish (Inflammable! Keep flames away). When the vessel is set

aside, the liquid gradually passes off in vapor (e-vapor-ates). The sulphur, however, gives practically no vapor at room temperature and remains as a residue in the form of crystals of rhombic outline in the bottom of the dish (Fig. 11). Here, again, physical properties have been utilized.

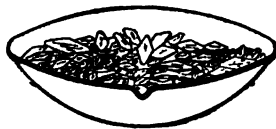
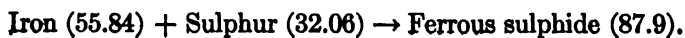


FIG. 11.

Since the physical properties of two substances are not changed by mixing, we have thus used the properties of the iron and sulphur so as to separate them once more. The iron is on the paper; the sulphur is in the dish.

**Combination of Iron and Sulphur.** — But iron and sulphur are capable of combining. If we alter the conditions by raising the temperature of some of the dry mixture, as we did in causing lead to rust rapidly, chemical union sets in. When we place some of the original mixture of iron and sulphur into a clean test-tube and warm it, we soon notice a rather violent development of heat taking place, the contents begin to glow, and what appears to be a form of combustion spreads through the mass. The heating employed at the start falls far short of accounting for the much greater heat produced. When these phenomena have ceased, and the test-tube has been allowed to cool, we find that it now contains a somewhat porous-looking, black solid. This material is brittle; it is not magnetic; it does not dissolve in carbon disulphide; and close examination, even under a microscope, does not reveal the presence of different kinds of matter. This substance is known to chemists as ferrous sulphide and, as we see, its properties are entirely different from those of the constituents.

In this connection we must not omit to notice that, as in rusting, a certain fixed proportion will be used in forming the compound. We find that, for 7 parts of iron, almost exactly 4 parts by weight of sulphur are required. If more iron is put into the original mixture, then some unused iron will be found in the mass after the action. If too much sulphur is employed, some may be driven off as vapor by the heat and all that remains, beyond the correct proportion, can be dissolved out of the ferrous sulphide with carbon disulphide. The sulphur which has combined with the iron, however, is no longer present as sulphur — it has no longer the properties of sulphur, and therefore cannot be dissolved out:



**Another Illustration: Mercuric Oxide.**— It has long been known that air contains an active and an inactive gas. The Chinese called them *yin* and *yang*, respectively. Mayow (1643–1679) showed that the active gas caused rusting, that it was absorbed by paint (really by the linseed oil) in “drying,” that it supported combustion of wood and sulphur, and that it is necessary to life, being absorbed by the blood from the air entering the lungs. It was not until later, however, that a pure specimen of this gas was obtained, and was recognized to be a special kind of gas different from ordinary air. The gas (later to be named oxygen) was made by Bayen from mercuric oxide, a bright red, rather heavy powder. When this substance is heated (Fig. 12), we find that a gas is given off, which is easily shown to be different from air, since a glowing splinter of wood is instantly relighted on being immersed in it. The gas is pure oxygen. We notice also during the heating that a sort of mirror appears on the sides of the tube. Apparently the vapor of some metal is coming off with the oxygen and condensing on the cool parts of the tube. As this shining substance accumulates it takes the form of globules, which may be scraped together. It is, in fact, the metal mercury, or quicksilver. If the heating continues long enough, the whole of the red powder eventually disappears, and is converted into these two products.

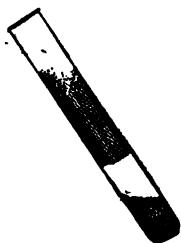


FIG. 12.



The extensive nature of the change in properties in this case is evident. It should also be observed that continuous heating is required to maintain this change in operation. It differs markedly from the iron and sulphur case in this respect. When the flame is removed, the evolution of oxygen ceases. The significance of this will appear shortly.

**Second Variety of Chemical Change: Decomposition.**— Bayen's experiment introduces to us a second, and very common kind of chemical action. The first variety was combination or union (p. 12). The second is called decomposition. It consists in starting with a single substance (here mercuric oxide) and splitting it into two (or more) substances, which differ in properties from the substance taken and from one another. Here, the red powder gave mercury, a liquid metal, and oxygen, a colorless gas.



**Third Illustration: Hydrogen from an Acid.** — If some sulphuric acid, a liquid, be added to 4–5 times its own volume of water, the acid dissolves, and **dilute sulphuric acid** is obtained. When zinc is added to the cold mixture, bubbles of a gas — hydrogen — form on the surface of the zinc and, when they become large enough, they rise to the surface and break. The gas burns, when set on fire, and differs, therefore, from air and from oxygen. The nature of the chemical change may be seen in the following abbreviated statement:

Zinc (65.37) + Sulphuric acid → Zinc sulphate + Hydrogen (2.016)

Sulphur (32.06)	Sulphur (32.06)
Oxygen (64.00)	Oxygen (64.00)
Hydrogen (2.016)	Zinc (65.37)

If sufficient zinc is used, the action will cease when all the acid, often called hydrogen sulphate, has been acted upon. The liquid can thus be poured away from the remaining zinc and can be partly evaporated. The liquid, when cold, then deposits crystals of zinc sulphate. This is a colorless substance, soluble in water, and therefore invisible until so much of the water has been driven off by boiling that the quantity of water which is left is not sufficient in amount to keep all the zinc sulphate in solution.

This chemical change is more complicated than are the two previously mentioned. The hydrogen leaves the sulphuric acid, and goes free, while the zinc takes its place, and combines with the sulphur and oxygen. The zinc is said to **displace** the hydrogen. Zinc is able also to displace, and liberate, metallic copper from cupric sulphate solution, and several other metals from their compounds.

**Third Variety of Chemical Change: Displacement.** — When a **simple substance** (here, the zinc) and a **compound** (here, sulphuric acid) **interact**, so that **another simple substance is set free**, and the **first simple substance takes the place of the second in the compound**, the action is called a **displacement**.

**Fourth Illustration: Salt and Silver Nitrate.** — The fourth illustration is taken purposely in order to illustrate the variety of ways in which chemical change may be carried out. It is the interaction of silver nitrate and sodium chloride (common salt). The substances may be recognized by the form of the crystals of which

they consist. The latter is composed of small cubes (Fig. 13), while the former presents a less familiar form geometrically (Fig. 14). Both substances are capable of being dissolved in water and, for this experiment, portions of each substance are shaken in separate

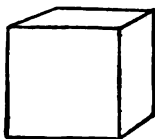


FIG. 13.

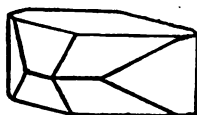


FIG. 14.

vessels with water, until none of the solid remains. When the solutions are now poured together, we observe that the clear liquids at once become opaque, and that a dense mass of white, solid material appears suspended in the mixture (Fig. 15). This white substance consists of an extremely fine powder without any observable crystalline form. We know at once that it must represent a new substance, since it would not have appeared had it been soluble in water like the two materials from which it was made. We continue adding the one liquid gradually to the other until no further formation of this solid takes place, and then stop. By filtration (Fig. 10), we obtain the insoluble material (the *precipitate*) upon the filter paper, and the clear liquid (the *filtrate*) passes through and is caught in the vessel below.

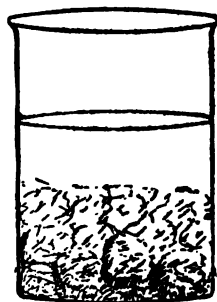


FIG. 15.

We are confronted with two possibilities: either both the original materials have come together to form one white insoluble material, or some other product (or products) may be present in addition to it. In the latter case, search must evidently be made in the liquid. By evaporating the *filtrate* in a suitable vessel (Fig. 11), we find that the second assumption represents the fact, for a considerable quantity of a white crystalline substance remains. The homogeneous character of this shows that there was but one product in solution, while the same property of the precipitate shows that there are but two products altogether.

The insoluble material is composed of silver and chlorine, and it is known as silver chloride. Like some other compounds of silver, it darkens on exposure to light, turning first purple and then brown,

and being decomposed by this agency into its constituents. The chlorine, a gas, escapes into the air, and a brown powder consisting of finely divided, metallic silver remains. The soluble solid, obtained from the filtrate, we recognize as identical with a mineral, sodium nitrate, which is found in Chile. Its crystals are rhombohedral (Fig. 69). They resemble cubes which have been slightly distorted by pressing inwards two opposite corners. This change presents several features which distinguish it from the previous ones: it is much more complex (see next section); it takes place in the presence of water; it requires no heating for its promotion; and the change is complete the instant the materials have been mixed, while the others required a good deal of time for their accomplishment.

**Fourth Variety of Chemical Change: Double Decomposition.**—The last illustration may be represented as follows, the numbers showing the relative weights as before:

Silver nitrate + Sodium chloride  $\rightarrow$  Silver chloride + Sodium nitrate

Silver (107.88)	Sodium (23.00)	Silver (107.88)	Sodium (23.00)
Nitrogen (14.01)	Chlorine (35.46)	Chlorine (35.46)	Nitrogen (14.01)
Oxygen (48.00)			Oxygen (48.00)

Here the constituents of both of the ingredients become separated (decomposition), and the products of this decomposition recombined cross-wise (combination). Thus, for example, the silver of one ingredient combined with the chlorine of the other. When **two compounds interact, so that each splits into two parts (called radicals), and the parts exchange partners in recombining**, the action is called a **double decomposition**.

**Fifth Variety of Chemical Change: Internal Rearrangement.**—When we encounter other chemical changes, we shall find the extent of the stride we have taken in this critical analysis of a few examples. It will then appear that the chemical changes of matter are not nearly so various in mechanism as we might have anticipated. In fact, there are few changes which cannot be placed in one of the four above described categories. Those that cannot be so placed belong to a **fifth variety** which, for the sake of completeness, may now be mentioned.

It occasionally happens, especially in the case of compounds of carbon (see Urea), that one single kind of material turns into another single kind of material. Nothing is added and nothing removed, yet the new substance has different properties in every respect from the

old. Most of those substances whose transformation is definitely assigned to this class contain several constituents, but a rough notion of this sort of chemical change may be obtained by considering the two forms of phosphorus. One of them is pale yellow in appearance, easily melted, and very easily ignited; the other is red, does not melt on being heated, and is difficult to ignite. The latter is made from the former by heating it continuously for some hours in a closed vessel at about 300°. As no material is taken up, the weight of the substance is unchanged, and yet, when the vessel is opened, the common phosphorus is found to have turned into the red variety. Now, we have seen that when substances have different properties they differ also in their constituent materials. Carrying out this idea, the hypothesis (or suggestion) has been made that, since here also the properties change, there must be some readjustment of the material, even in cases like this. Hence, we designate changes of this kind **internal rearrangements**. The composition of the material is unaltered, so we suppose its constitution to have become different. If the chemists ever decide to regard the change of water into ice or steam as a chemical phenomenon, all changes of state of aggregation would be placed in this fifth class. It is here only that the boundary between physics and chemistry is at present difficult to define.

**Characteristics of Chemical Change.**—The different varieties of chemical change can now be tabulated for reference:

1. **Combination** (pp. 12, 16 \*): **Two (or more) substances give one substance.**
2. **Decomposition** (p. 17): **One substance gives two (or more) substances.**
3. **Displacement** (p. 18): **One simple substance and one compound substance give one simple substance and one compound.**
4. **Double Decomposition** (p. 20): **Two compound substances give two compounds.**
5. **Internal rearrangement** (p. 21): **One substance gives one substance.**

The **characteristics of chemical change**, thus encountered, are, therefore, (1) that the change can almost always be classified under one of the five varieties just mentioned, and (2) that each of the substances used or produced has a distinct set of specific physical properties of its own, by means of which it can be recognized.

\* See footnote on p. 14.

**Simple and Compound Substances.**—If we place before a physicist samples of iron, ferrous sulphide, and sulphur, he will report that there are three absolutely distinct *substances* represented, because they show three different sets of physical properties. A chemist, on the other hand, while admitting the accuracy of the report, in view of the criterion used by the physicist, which indeed he uses himself (*cf.* p. 4), will insist on adding that there are only two perfectly distinct *kinds of matter* in the set, because he can make the second from matter furnished by the other two. The same sharp contrast in the points of view arises when mercury, mercuric oxide, and oxygen, or any similar set of substances, is submitted to the same two tribunals. In a sense, chemistry reduces the kinds of different matter to a much smaller number than does physics or any of the other sciences, and so it is the final authority in all questions involving matter. By the chemist, dozens of physically distinct substances are regarded as closely related because they all can be made with iron, or when decomposed give it; hundreds are alike in that sulphur enters into their composition; thousands are compounds of oxygen. In fact, the number of kinds of matter which are perfectly distinct in the strictly chemical point of view is quite limited.

The conception contained in the last statement was not reached until centuries of effort had been spent in trying to make gold out of pyrite (a shining yellow mineral), or silver out of lead. The first to put our modern view into definite language was Lomonossov. Later, and independently, it was stated very clearly by Lavoisier in his *Traité de Chimie* (1789). Lomonossov never believed in phlogiston (p. 9), although all his contemporaries did, and the later investigations of Lavoisier finally overthrew this absurd hypothesis and caused the general acceptance of the view that chemical changes involved only combination or decomposition of different kinds of matter. His work showed, also, that decomposition had its limits. Mercuric oxide could be decomposed into mercury and oxygen, but no means was found of breaking these up in turn and producing any fresh substances from them. The kinds of matter composing these simple materials he named **elements**. The element is to be regarded as an ultimate chemical individual just as the substance is the physical individual. **The definition of an element is therefore: a distinct species of matter which we are not able, at will, to decompose into, or to make by chemical union from, other substances.**

The caution which prompted Lavoisier to use, as he did, the words "has not yet been," was justified by the fact that several substances,

in his time regarded as elementary, were afterwards shown to be compound. Thus, quicklime was a simple substance until Davy, in 1808, prepared the metal calcium and showed that quicklime was a compound of this metal with oxygen. Hence, we do not say that the substances regarded as simple **cannot** be decomposed, but only that they are substances which we "are not able" (at present) to decompose.

The phrase "at will" is also important. Radium (*q.v.\**) cannot be decomposed at will, but it undergoes continuous "disintegration," producing the elements helium and lead. We can neither hasten, retard, nor stop this spontaneous decomposition.

Recent discoveries, showing that the atoms of which elementary substances are composed are made up of different numbers of particles of positive and negative electricity, have revived the idea that it may be possible to make one element out of another. If this should be accomplished, as it soon may be, it may be necessary radically to revise the definition just given.

The chemist's work is, at present, directed wholly by the thought that the individual element (the matter), after combination, is still present in the compound in some form which is at least *quasi*-discrete. The readiness of the element to be released once more under suitable conditions seems to favor this point of view.

**A compound is a substance which can be made by chemical combination of, or can be decomposed into, two or more substances.**

**Elements.** — The word element is used in two senses. It is applied to the simple substance. Thus we speak of "the element iron," meaning the metal iron. It is applied also to the iron-matter contained in ferrous sulphide or in ferric oxide. The reader should note that it is correct usage to speak of the *element* iron and the *element* sulphur in ferrous sulphide, but a chemist would never say that this compound contained the *simple substances* iron and sulphur. If he did, we should understand him to mean that it was a mixture, and we should expect parts of the material to be magnetic like iron, and other parts to be yellow and soluble in carbon disulphide, which is not the case. In the same way the *name* of an element (such as "iron") is applied both to the material in combination and to the free substance. Thus "iron" may mean free, uncombined, metallic iron, or iron-matter in some compound. The sense in which the word is employed must be inferred from the context or circum-

\* See footnote on p. 14.

stances. When a chemist speaks, as he sometimes does, colloquially, of "iron" in a drinking water, for example, we know at once that he refers to iron in the form of some compound, for metallic iron does not dissolve in water and, if it did, would quickly turn into rust or some other form of combination.

The word **element**, then, means **one of the simple forms of matter, either free or in combination.**

In formally describing a body or specimen, the chemist always avoids the ambiguity just referred to *by naming the components, i.e., the substance or substances it contains.* He assumes that the nature and constituents of these substances will be known to anyone hearing or reading the description. If he says the body contains zinc and sulphur, it is understood that the body is a mixture of these simple substances. If it contains these elements in combination, the chemist would report that it was sulphide of zinc.

**The Common Elements.** — Thousands of different compound substances are known but, when they are decomposed, it is found that the number of different *elements* contained in them is not great. As we have said, dozens of substances contain iron, hundreds contain sulphur, thousands contain oxygen. In fact, by combining a limited number of simple substances, two, three, or four together, in varying proportions by weight, an almost unlimited number of different compound substances could be produced.

The list of the elements appears on the inside of the cover, at the end of this book, and contains about eighty names. Of these, a large number are rare, and seldom encountered. More than 99 per cent of terrestrial materials is made up of eighteen or twenty elements and their compounds. Only about twenty elements occur in nature in their simple, uncombined condition. Three-fourths of the whole number are found in combination exclusively, and must be liberated by some chemical action.

Taking the atmosphere, all terrestrial waters, and the earth's crust, so far as it has been examined, F. W. Clarke has estimated the plentifulness of the various elements. The first twelve, with the quantity of each contained in one hundred parts of terrestrial matter, are as follows:

Oxygen.....	49.85	Calcium.....	3.18	Hydrogen.....	0.97
Silicon.....	26.03	Sodium.....	2.33	Titanium.....	0.41
Aluminium.....	7.28	Potassium.....	2.33	Chlorine.....	0.20
Iron.....	4.12	Magnesium.....	2.11	Carbon.....	0.19

Thus oxygen accounts for nearly one-half of the whole mass. Silicon, the oxide of which when pure is quartz and in less pure form constitutes the ordinary sand, makes up half of the remainder. Valuable and useful elements, like gold, silver, sulphur, and mercury, are among the less plentiful which, all taken together, furnish the remaining one per cent.

**Warnings.** — A **substance** (p. 4) must be defined by the constancy of its physical properties, and not by saying that it is "a material of some specified, definite composition."\* We know many sets of anywhere from two to a dozen or more substances with the very same composition, yet the members of each set have entirely different physical properties, and often are entirely different in chemical behavior. Thus, red and yellow phosphorus are both composed entirely of phosphorus, yet differ markedly in physical properties. Again, urea and ammonium cyanate have the same composition, but differ in physical properties and, besides, belong chemically to entirely different classes of substances. The first is basic in nature, the second a salt.

Again, a **substance** must not be defined as "a *portion* of matter," for that is the definition of a body (p. 7). A substance is a *variety* or *species* of matter, and not any one portion or specimen. A crystal of salt is "a portion of matter," and a specimen of the substance, but the phrase "the *substance* salt" covers *all* known and unknown specimens of salt, and even not-yet-existent specimens which may be formed in the future.

Beware of defining a **compound substance** (p. 12) as being "composed of two or more simple *substances*." That is a definition of a mixture, and such a product would show two or more kinds of matter with different properties. A compound substance contains only one substance, and every particle has the same physical properties as every other particle. A compound substance might be defined as "a substance composed of two or more elements." This definition, however, is academic, and gives no clew to how a compound is shown to be such. Chemistry is an experimental subject, and all definitions should be stated in terms of the *experimental method of classifying a given case*, as is done in the definition given above (p. 12).

\* In chemistry, the word **composition**, when applied to a substance, refers both to the elements present in the compound and to the proportions by weight in which they are present.



**Summary.** — In the latter half of this chapter we have learned: (1) that physical properties are utilized in manipulations, like filtration and evaporation, as well as for identifying substances; (2) that practically all chemical changes can be classified under one of five varieties; (3) that, while there are very many substances, there is a very limited number of entirely different kinds of matter (elements).

**Exercises.\*** — 1. Take one by one the words or phrases printed in black type and the titles of the sections in this chapter, and endeavor to recollect what you have read about each. In each case try, (a) to recall the meaning and to state it in your own words; (b) to recall the facts associated with, and the reasoning which led up to the point in question; (c) to recall examples illustrating the conception and to apply the conception in detail to each example. Whenever memory fails to give a perfectly clear report of the matter in hand, the text must be read and re-read until the essential point can be repeated from memory.

Use the same method in all future chapters. A useful practice is to employ a pencil as you read and to underline systematically all the important facts and statements, and then to go back and apply to each marked place the process described above.

2. Define the following terms: density, tenacity, melting-point, brittleness, specific physical property, pure body, vacuum.

3. Is it logical to say "pure substance"?

4. Why do we decide that granite is a mixture and iron a single substance?

5. Do the statements in the text indicate that air is a mixture or a compound?

6. What weight of oxygen would be required to turn 25 grams of lead into oxide of lead?

7. Make a list of the technical words we have defined, and place the definitions opposite to each.

8. What weight of tin would be contained in 15 grams of oxide of tin?

9. If any of the following are mixtures, mention the facts which

\* The exercises should in all cases be studied with minute care. They not only serve as tests to show that the chapter has been understood, but very frequently also call attention to ideas which might not be acquired from the text alone, or (as in Nos. 11, 12) assist in elucidating ideas given in the text which, without the exercises, might not be fully grasped.

show them to contain more than one substance: (a) muddy water, (b) an egg, (c) milk, (d) a candle, (e) a cake of soap.

10. What are the two most direct ways of showing a substance to be a compound? Illustrate each.

11. If we say that quicklime contains calcium (p. 23), do we mean the element or the simple substance calcium?

12. What physical properties are used, (a) in filtration, (b) in evaporation, (c) in the separation and identification of the products from heating mercuric oxide (p. 17)?

13. Take the chemical action on p. 16, par. 3, and enumerate the physical properties of the substances before and after the chemical change.

14. Discuss in detail the experiments with zinc and sulphuric acid (p. 18), and with silver nitrate (p. 19), showing what specific properties were used for separating and identifying the products, and how they answered the purpose. Which methods of manipulation were employed in the second experiment, and which method was used, essentially, in the first?

15. Define the following terms, and find illustrations of each, other than those given on p. 6: mixture, physical component, chemical constituent.

16. What (a) elements and (b) substances are contained in an aqueous solution of sodium nitrate? Would it be correct to say that the simple substance oxygen is contained in it? What then is the difference in meaning between the terms "element, oxygen" and the "simple substance oxygen"?

17. What explanation was given, (a) of the disappearance of mercuric oxide when heated, (b) of the absence of iron and sulphur, as substances, from ferrous sulphide? Which of the three kinds of explanation was used in each case?

## CHAPTER II

### ENERGY IN CHEMICAL CHANGE. PHYSICS IN PRACTICAL CHEMISTRY

STUDY of the four typical chemical changes described in the last chapter may now be resumed, in order to see whether anything further of a general nature is characteristic of such phenomena.

*Physical Concomitants of Change in Composition.* — We recall at once that a prominent feature of the union of iron and sulphur (p. 16) was the **heat** which, as shown by the glow spreading through the mass, seemed to be **developed** after the action was once started. It is found that many chemical changes are like this one, in exhibiting simultaneously the production of very perceptible amounts of heat. The burning of wood and of coal are examples. On the other hand, the decomposition of mercuric oxide, as was pointed out (p. 17), owed its continuance to the persistent application of heat, and ceased so soon as the source of heat was withdrawn. Here, apparently, **heat was consumed** during the progress of the change, and the chemical action was limited by the amount of heat supplied. The **production or consumption of heat** may, therefore, be a feature of chemical change.

In the iron and sulphur case, as in other chemical actions where the heat developed is great, **light also was given out**. In the last of the actions, on the other hand, we obtained a substance (silver chloride), which may be kept for any length of time in the dark, but, by the action of sunlight is broken up into its constituents (p. 19). It would appear, therefore, that **light may be given out or used** in connection with chemical change. Noting these facts stimulates us to look for other similar concomitants of change in composition.

If we dip two wires from a battery or dynamo into a solution of nitrate of silver (Fig. 16), such as was used in the fourth experiment, we observe the instant production of a coating of silver on the negative wire. By preparing the solution properly and allowing the **electricity** to flow through it for a sufficient length of time, all of the compound can be decomposed and all its silver deposited. It is

needless to say that this release of the silver from chemical combination, and liberation of the metal at the electrode, goes on only so long as the current of electricity is employed, and that electrical energy is consumed in the process. Very many substances can be decomposed in this way.

The inverse of this is likewise familiar. If we place in dilute sulphuric acid a stick of the metal zinc (p. 18), we find that a gas is given off rapidly (Fig. 17), that the zinc gradually dissolves, and

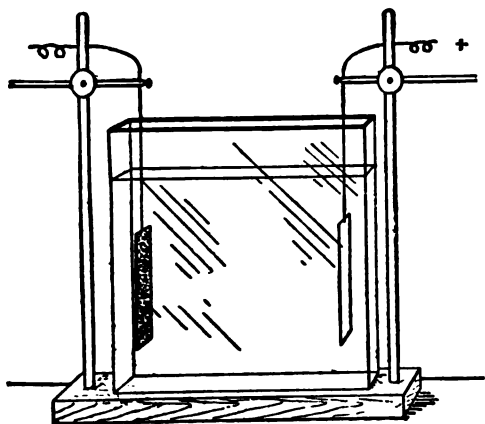


FIG. 16.

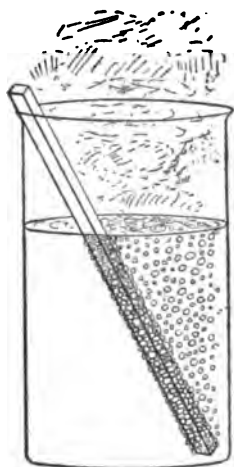


FIG. 17.

that a large amount of heat is developed. A thermometer immersed in the vessel will show that the temperature is rising. If much pulverized zinc is used, the liquid may even rise spontaneously to the boiling-point. This form of the action produces heat. If, however, we attach the same stick of zinc to a copper wire, and immerse it and a plate of platinum simultaneously in the acid (Fig. 18), then a galvanometer, with which the wires are connected, shows at once the passage of a current of electricity round the circuit. Exactly the same chemical change goes on as before (p. 18). The sole difference is that the gas appears to arise from the surface of the platinum. It is easy to show, however, that the platinum by itself is not acted upon by dilute acids, and, in this case, undergoes no change whatever; it serves simply as a suitable conductor for the electricity. Here, then, in place of the heat which the first plan

produced, we get electrical energy. The arrangement is, in fact, a battery-cell, for a battery is a system in which a chemical action, which would otherwise give heat, furnishes electricity instead. Thus, **electrical energy may be consumed or produced in connection with a change in composition.**

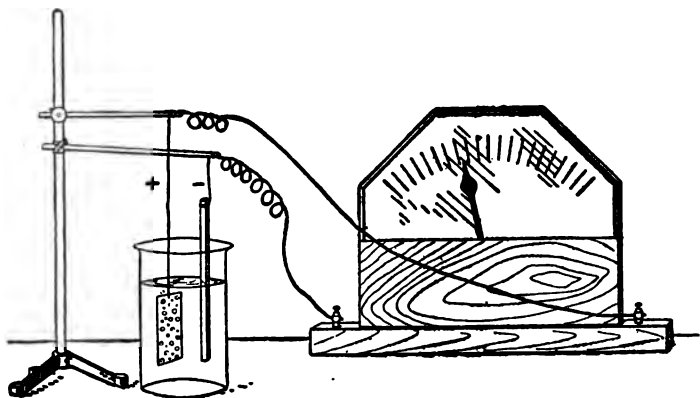


FIG. 18.

Even violent rubbing in a mortar, in the case of some substances, can effect an appreciable amount of decomposition in a few minutes. In this way silver chloride can be separated into silver and chlorine, just as by light. It is the **mechanical energy** which is the agent, and part of it is *consumed* in producing the change, and only the balance appears as heat. Conversely, the *production* of mechanical energy, as the result of chemical change, is seen in the behavior of explosives and in the working of our muscles. Thus, **mechanical energy may be used up or produced in chemical changes.**

Summing our experience up, we may state that no change in composition occurs without some concomitant, such as the production or consumption of heat, light, electrical energy, or, in some cases, mechanical energy. It must be noted that **these phenomena are an essential part of the chemical change**, and are as important as is the production of new substances which goes on at the same time. We must, therefore, give attention to both.

**Classification of the Concomitants of Change in Composition: Energy.** — The problem of classifying (*i.e.*, placing in a suitable category) things like heat, light, and electricity has occupied

much attention. They do not possess mass. In all chemical changes, one of these natural concomitants is given out or absorbed, sometimes in great amount, yet in none is any alteration in weight observed. Nor may these concomitants be overlooked, simply. A conception is a real thing; a religious belief may be most real and potent. There are many things which are real, although they are not affected by gravitation. In the present instance we reason as follows:

A brick in motion is different from a brick at rest. The former can do some things that the latter cannot. Furthermore, we can easily make a distinction in our minds. The brick can be deprived of the motion and be endowed with it again. Thus, we can get the idea of motion as a separate conception. Similarly, we observe that a piece of iron behaves differently when hot, and when cold, when bearing a current of electricity, and when bearing none. We conceive then of the brick or the iron as having a certain amount and kind of matter which is unalterable, and as having motion, heat, or electricity added to this or removed. Thus, we describe our observations by using two categories, one of which includes the various kinds of **matter**, and the other, various things whose association with matter seems to be invariable and is often so conspicuous.

At first sight, these concomitants of matter seem to be quite disparate. But a relation between them can be found. If the heat of a Bunsen flame or of the sun is brought under a hot-air motor (Fig. 19) violent motion results. Again, if the motor is connected with a dynamo, electricity may be generated. Still again, if the current flows through an incandescent lamp, heat and light are evolved. Conversely, when motion is impeded by a brake, heat appears. When a current of electricity is run through the dynamo, motion results. But the most significant facts are still to be mentioned. The heat absorbed by the motor is found to be greater when the machine is permitted to move and do work, than when it is not. Thus, we find that when work is done by the motor some heat disappears, being transformed into work. Similarly, when the poles of the dynamo are properly connected and electricity is being produced, and only then, motion is used up. This is shown by the

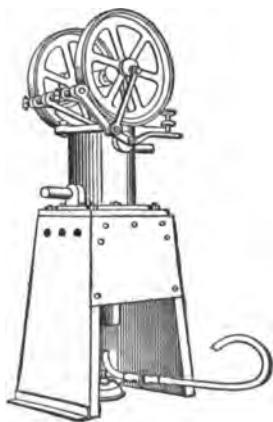


FIG. 19.

effort required to turn the armature under these circumstances, and the ease with which it is turned when the circuit is open. So, with a conductor like the filament in the lamp, unless it offers resistance to the current and destroys a sufficient amount of electricity, it gives out neither light nor heat. Finally, motion gives no heat unless the brake is set, and effort is then demanded to maintain the motion. These experiences lead us to believe that we have here a set of things which are fundamentally of the same kind, for each form can be made from any of the others. We have, therefore, invented the conception of a single thing of which heat, light, electricity, and motion are forms, and to it we give the name **energy**: **energy is work and every other thing which can arise from work and be converted into work** (Ostwald).

Closer study shows that equal amounts of electrical or mechanical energy always produce equal amounts of heat. There is never observed any loss in transformations of energy, any more than in transformations of matter. Hence, J. R. Mayer (1842), Colding (1843), and Helmholtz (1847) were led independently to the conclusion that **in a limited system no gain or loss of energy is ever observed**. This brief statement of the results of many experiments is called the **law of the conservation of energy**.

A current form of this law, namely, that "the total amount of energy in the universe is a constant quantity," is open to the same objection as the correspondingly flamboyant form of the law of conservation of mass criticized later (p. 52). It has a more effective sound than the one we have given. Unfortunately, it is not only immensely in excess of any statement that present results of scientific work can justify, but is probably far beyond the limits of possible scientific observation. Scientific statements of fact can never err by being too conservative.

**Matter and Energy as Concepts, and Definitions of the Latter.** — The foregoing paragraphs about energy bring up the question of its relation to matter. This relation can be made clear only by a somewhat elaborate discussion of our fundamental conceptions.

The only real, first-hand knowledge which we possess, is that of our states of consciousness. All else, consisting, for example, of the way in which we interpret and describe our experience, is constructed out of our heads, so to speak. Now, we become aware of certain things which we call sensations, and seek to construct a mode of correlating and describing them. Our universal habit is to speak as if they were produced by something outside our minds, and so we begin the manufacture of an external universe. In course of doing this, we encounter some things which seem to occupy no particular space, which move from object to object, and possess no weight. One of these affects our eye, or a piece of

chloride of silver, for example, yet escapes touch, and passes through glass almost as easily as through a vacuum. After consideration of our experience with this sort of thing, some of which has been detailed above, we decide that we shall posit the existence of energy.

Other things we encounter appeal to the sense of touch and seem to possess more definitely located qualities, including weight. Another conception is needed to account for these; so we establish the category of matter.

Thus, we make shift to describe our sensations by the help of these two constructs, much as in analytical geometry we describe the location of a point by means of two coördinates. Energy and matter are, therefore, products of thought and not, primarily, objective realities. In chemistry, however, we always speak of them objectively. Historically, the order in which these two concepts were named and defined was the opposite of that in which they stand above. Yet attempts to organize a conception, corresponding to energy, in response to a need of which thinkers were conscious, were not wanting before the nineteenth century opened. To go no further back than the days of phlogiston, we can easily perceive a certain resemblance between this concept and that of energy. The idea that heat was an "imponderable" had its origin much earlier, and shows the existence of the same effort to find a second fundamental conception different from matter.

There is much confusion of thought in many of the current definitions of energy. For example, it is often said to be "that which causes change in matter." This definition is not easy to bring into harmony with common experience in chemistry. Thus, when heat is applied to mercuric oxide, the change follows. But with iron and sulphur, the union of the two substances is a condition antecedent to the evolution of heat. It is as often true that change in matter causes the manifestation of energy as the reverse. Matter and energy are on the same plane. They are conceptions used jointly in describing what we observe. Neither is secondary to the other. We do not consider any particular one of the coördinates in geometry as secondary to the other, or as being affected by the other.

The theory of chemical potential and of the factors of energy (*q.v.*) seeks once more to ascribe the tendency to change (physical or chemical) in matter to the state of the energy associated with it. It is, therefore, incidentally, so constructed as to favor the definition just given.

The definition that "matter is the vehicle of energy" is obviously just as difficult to harmonize with the above mode of deriving the two conceptions. One axis is not spoken of as the vehicle of the other in geometry.

The innate desire to reduce our distinct categories to the smallest possible number may be seen in the history of this subject. The ancients sought the amalgamation of the two by regarding heat and light as *imponderable* forms of matter. It is now believed that the one conception of energy is sufficient, and that matter may be put into the same category as being composed of minute particles of electricity (positive charges and electrons).

The conception of *ether* was devised because those of matter and energy did not suffice for the description of all the phenomena of light. It is on the same



plane with matter and energy. Lord Kelvin's effort to reduce the three categories to two (energy and ether) by assigning the rôle of matter to vortices in the ether is familiar to students of physics.

***Application of the Conception of Energy in Chemistry.*** — At first sight it looks as if the statement that energy is conserved is not applicable in chemistry. Heat and electricity, for example, seem to be produced and consumed, in connection with changes in composition, in a mysterious manner. We trace light in an incandescent lamp back to the electricity, and this in turn to the mechanical energy, and this again to the heat in the engine. But what form of energy gave the heat developed by the combustion of the coal under the boiler, or by the union of iron and sulphur in our illustration (p. 16)? Since we do not perceive any electricity, light, heat, or motion in the original materials, and yet wish to create an harmonious system, we are bound to conceive of the iron and the sulphur, and the coal and the air, as containing another form of energy, which we call **chemical or internal energy**. Similarly, when heat is used up in decomposing mercuric oxide, or light in decomposing silver chloride, we regard the energy as being stored in the products of decomposition in the form of internal energy.

***The Actual Quantities of Different Kinds of Energy which may be Obtained from a Fixed Amount of One Kind.*** — It will render all the above clearer if we give some numerical illustrations: A kilogram of water after falling (in a vacuum) 428 meters (about one-fifth of a mile), under gravity, possesses 428 kilogram-meters of mechanical (kinetic) energy. When the motion is arrested, the energy of motion is transformed into heat and raises the water one degree centigrade in temperature. We describe this amount of heat as 1000 calories (small); that required to warm one gram of water one degree (at 15°) being called one calorie. A kilogram of any other falling material would give the same amount of heat (1000 cal.), although, of course, if its specific heat were smaller than that of water, the temperature to which it would be raised would be higher, and *vice versa*.

Here the acting force is the attraction of gravitation, which is a special case. In absolute units, 1 g. falling 1 cm. generates energy enough to do 981 ergs of work. So that the thousand grams falling 428 meters (42,800 cm.) generates

$$1000 \times 42,800 \times 981 = 42,000,000,000 \text{ ergs of energy.}$$

The erg being so small, we often use the joule (= 10,000,000 ergs). This amount is the same as 4200 joules.

Now, any body of the same mass, moving with the same final velocity, however set in motion, will also possess the same energy and give 1000 cal. The final

velocity in the above case is  $\sqrt{2}$  gs. = 9164 cm. per second. The energy of motion ( $\frac{1}{2} mv^2$ ) of one thousand grams of matter moving with this velocity is  $= \frac{1}{2} \times 1000 \times (9164)^2 = 4200$  joules, as before. If the source of mechanical energy were a hot-air motor (or an engine) of one horse-power, then, since one horse-power represents a development of 746 joules per second, the 4200 joules of energy would be produced in about  $5\frac{1}{2}$  seconds by this means.

If, instead of being turned into heat, all the energy of motion had been converted into electricity, the quantity of the latter would have illuminated a 50-watt incandescent lamp for 84 seconds (= 1.4 minutes). Such a lamp requires 50 joules per second of electricity and, therefore, in 84 seconds uses up the  $50 \times 84 = 4200$  joules of energy. As an engine of 1 horse-power produces this amount of energy every  $5\frac{1}{2}$  seconds, such an engine, if none of the energy were lost, could maintain nearly 15 lamps of this kind.

Finally, if the 4200 joules of electrical energy were applied to decomposing nitrate of silver in ordinary aqueous solution, it would liberate  $6\frac{1}{2}$  grams (about  $\frac{1}{8}$  oz.) of silver from combination.

**Considerations Connected with Internal Energy: Free Energy.** — These conclusions compel us, for the sake of consistency, to think of all our materials as repositories of energy as well as of matter, each of these constituents being equally real and equally important. A piece of the substance known as "iron" must thus be held to contain so much iron matter and so much internal energy. So ferrous sulphide contains sulphur matter, iron matter, and internal energy. Thus, by a *substance* we mean a distinct species of matter, simple or compound, with its appropriate proportion of internal energy. During the progress of a chemical change, like the union of iron and sulphur, the chemical energy of the system diminishes and heat is liberated, or, when arrangements are made for utilizing the energy, work of some kind is done.

The energy which becomes available as the result of a chemical action, and is free to be converted, say, into electrical energy, is called the **free energy** of the action. Now, it must be noted that the free energy, measured by work done, is not, in general, the equivalent of the heat developed by the natural progress of the change. Often the amounts are nearly equivalent, although never absolutely so. But frequently they are very different. When the free energy available for conversion into work is greater in amount than the heat of the reaction, as it often is, the difference is taken up from the heat of the surroundings during the progress of the change, and the vessels and objects in contact with the interacting bodies become colder. Thus phosphonium chloride (*q.v.*) decomposes spontaneously into two gases, phosphine and hydrogen chloride, and ammonium carbonate gives off ammonia gas, while heat is absorbed in both cases. Work can be done by both these actions, although, so far as heat is concerned, not only is none of this

form of energy liberated, but a certain amount of it is absorbed. Conversely, when the heat of reaction is greater than the equivalent of the free energy, then, along with the energy which would be used to do work (for example, by employing the action as a source of electricity), a certain amount of heat which cannot be transformed into work will be given to the surroundings. It thus appears that the substances which we handle are not only repositories of energy, but, when brought together, also play the part of machines for transforming energy which they take from or give to the surroundings.

***The Third Characteristic of Chemical Change.*** — In the course of this discussion it has become clear that it is a characteristic of a chemical change that, besides a change in that state of the *matter*, there is always an alteration in the amount of internal energy in the system. This alteration involves the production of internal energy from, or the transformation of internal energy into, some other form of energy.

***Exothermal and Endothermal Changes.*** — The energy liberated in a chemical action appears most commonly in the form of heat. Changes which, like the union of iron and sulphur (p. 16), are accompanied by the liberation of heat are called **exothermal** actions. Those in connection with which heat is absorbed, like the decomposition of mercuric oxide (p. 17), are known as **endothermal**.

It should be noted here that neither the production nor the absorption of heat is an exclusive mark of chemical change. Physical changes are all likewise accompanied by the liberation or consumption of energy. Thus, water, in evaporating, absorbs heat, and liquids on solidifying, or often even when simply mixed with other liquids, give out heat.

***Practical Importance of Energy in Chemical Change.*** — The absorption or liberation of energy accompanying a chemical transformation of matter is often, of the two, the more important feature. We do not burn coal in order to manufacture carbon dioxide gas. We are glad to get rid of the material product through the chimney. It is the heat we want. We do not employ zinc in batteries with the object of making zinc chloride or zinc sulphate. So we use the electrical energy, and throw the material products away when we refill the battery jars. It is the same with burning illuminating gas or magnesium powder when we want light, and with eating food, which we do, chiefly, to get energy to sustain our activity. We do not run electricity for hours into a storage battery in order to make

a particular compound (lead dioxide, for example), but in order to save and store the energy for future use. In industry and life, fully half the total amount of chemical change involved, is set in motion by us, solely on account of the energy changes it involves.

As will be seen in the following section, observation of the amount of the energy absorbed or liberated in chemical changes is also of the greatest importance in the *scientific* study of chemical phenomena.

**Chemical Activity.** — Other things being equal, actions in which there is a relatively large loss of internal energy and, therefore, usually, a considerable liberation of heat or electrical energy, proceed rapidly; that is to say, in them a large proportion of the material is changed in the unit of time. Those in which less free energy is transformed proceed, in general, more slowly. The speed of the chemical change, and the quantity of energy available because of it, are closely related. Now, we are accustomed to speak of materials which, like iron and sulphur, interact rapidly and with liberation of much energy as “chemically active.” Thus, **relative chemical activity** may be estimated:

1. By **observing the speed of a change** (see Speed of chemical actions), or, in many cases,
2. By **measuring the heat developed** in the course of the action (see Thermochemistry), or,
3. By **ascertaining the electromotive force of the current the change gives**, when arranged in the form of a battery-cell (see Electromotive chemistry).

These different methods will be discussed in later sections. It should be noted here, however, that the speed of a given action may be enormously affected by conditions (see, for example, Catalysis), and that, therefore, great caution is required in inferring relative activities from observed differences in the speeds of several actions. Thermal measurements are also often misleading. This is evident from the fact that an action may be able to do work, even although heat energy is absorbed during its progress. Thus, phosphonium chloride (*q.v.*) decomposes of its own accord into phosphine and hydrogen chloride, although it absorbs heat from surrounding objects in doing so. **The electrical method of measuring the available (free) energy, and therefore the true affinity, is in general the most trustworthy.**

It is evident that the chemical activity of a given substance will not be the same towards all others. Thus, iron unites much more

vigorously with chlorine than with sulphur and, with identical amounts of iron, more heat is liberated in the former case than in the latter. With silver, sodium, and many other substances, iron does not unite at all. One of the tasks of the chemist is to make such comparisons as this (see Specific chemical properties, p. 86): Evidently, the substances containing the most internal energy will be in general the most active.

**The "Cause" of Chemical Activity.** — The reader will undoubtedly be inclined to inquire whether we can assign any cause for the tendency which substances have to undergo chemical change. Why do iron and sulphur unite to form ferrous sulphide, while other pairs of elements taken at random will frequently be found to have no effect upon one another under any circumstances? This question is so likely to occur to the reader that it should be dealt with at once. The answer is that we do not know. Questions like this have to go without answer in all sciences. What is the cause of gravitation? We know the facts which are associated with the word — the fact that bodies fall towards the earth, for example — but *why* they fall we are unable to say. So, with chemical change, we can state all the facts we know about it, that is, we can tell *how* the change takes place, but even then we cannot say *why* it takes place.

The words "affinity" and "attraction" are sometimes advanced as if they supplied some explanation of chemical activity. Now, we have seen that an explanation in science (p. 10) is a description of the details of some process, either in terms of known facts, or by the use of some imaginary but plausible and helpful machinery. Here no facts are known. Even imaginary machinery has not yet been conceived by any one. So that these terms are words simply, and do not meet either of the conditions required of an explanation. They are names for "the tendency to undergo chemical change," and that is all.

All nouns, such as table or book, are general terms applicable to many more or less various individuals. Some special nouns are used in chemistry. For example, *affinity* names the tendency to undergo chemical change, and distinguishes this tendency by name from cohesion, or the tendency to unite physically. *Catalysis* names a kind of chemical change in which some specific substance must be present, and influences the other substances by contact with them, yet itself undergoes no change. *Dissociation* names the kind of chemical change in which decomposition occurs with rise in temperature, and recombination when the temperature falls. But none of these terms, as such, is an explanation. It does not explain the concussion of two railway trains to name it a collision.

Of course, if we have some genuine explanation, applicable to all the other known cases of a class, any newly discovered example falls heir at once to this

explanation. This would be true of a dissociation, where the kinetic theory and the law of mass action describe the details of all such phenomena. Here the explanation lies, not in the name, but in the knowledge we have of other instances of the same behavior. The name, of course, suggests the whole theory, if such a theory exists. But with affinity, or the tendency to enter into chemical action, we have no theory for any of the samples of the class. We are entirely ignorant as yet of the details of its mode of operation, equally so in every case, and, in fact, know nothing at all about it save that affinity exists and that we can measure its intensity. So the name cannot remind us of any explanation, for none has been suggested.

As words, the best one can say of them is that they are rather unfortunately chosen. Affinity suggests kinship, sympathy, or affection. But the suggestion that such human emotions control the behavior of iron and sulphur is too wild and too remote from common sense to furnish any assistance. Attraction hints at some preëxisting bond of a material kind which draws the substances together, for we cannot conceive of action at a distance without some intervening medium of communication. But we have no other evidence of the existence of an instantaneously adjustable harness capable of drawing materials into chemical action. It is harder to reduce this idea to comprehensible shape than to do without it.

If we are still inclined to think that these are more than class-words, and do suggest some explanation, we have only to carry the same idea further to be landed in absurdity. Using similarly crude analogies, we might suppose that the elements were guided by scent, like dogs, or by sight, like birds, or by feeling, like fish, and so on *ad infinitum*, and forget that the fact itself was after all much simpler than the explanation. Affinity is simply a fanciful name for a real thing.

**"Cause" in Science.**—The word "cause" was employed in the heading of the last section, and it will be observed that no cause was found. This is the invariable rule in physical or chemical phenomena. We know of no causes, in the sense in which the word is commonly employed.

The word cause has only one definite use in science. When we find that thorough incorporation of the three materials is needed to secure good gunpowder, we say that the intimate mixing is a cause of its being highly explosive. By this we simply mean that intimate mixture is a *necessary antecedent* of the result. A cause is a condition or occurrence which always precedes another condition or occurrence.

Misuse of the word "cause" is frequent. The law of gravitation is not the cause of the behavior of falling bodies. It is simply a condensed narration of the facts about falling bodies, and was made long after the first bodies fell. Affinity, or the tendency to interact chemically, is the imagined antecedent of chemical change. Such causes, if we call them causes at all, are invented by way of supplying antecedents to things that appear to lack them, that our sense of symmetry may be satisfied withal. They are occasionally useful. But the less fiction we

employ in the science, the less will be the danger that the student will mistake fictions for facts, or even fall under the delusion that it is a habit of science to spend more thought in making gratuitous assumptions than in ascertaining facts.

### PHYSICS IN PRACTICAL CHEMISTRY

**List of Important Specific Physical Properties.** — We have seen that, to the chemist, knowing the physical properties of all substances is very important. By means of the properties, he recognizes and describes all the bodies he studies. It may be well, therefore, here to give a **list of the more important properties**, most of which have been mentioned in connection with the illustrations we have used.

In the case of **solids**, the chief physical properties the chemist uses are: **color**, **odor**, **crystalline form**, **hardness** (Appendix II), **solubility or non-solubility** in water and occasionally other liquids, the temperature at which the substance melts (**melting-point**), the **density**, and the **conductivity for electricity**.

In the case of **liquids**, he notes the temperature at which the liquid boils (**boiling-point**), the **density**, the **mobility**, the **odor**, and the **color**.

Finally, in the case of **gases**, the properties commonly mentioned are the **color**, **taste**, and **odor**, the **density**, the **solubility** in water, and the ease or difficulty with which the gas can be **liquefied** (see critical temperature).

For example, sulphur is yellow, has little odor, crystallizes in the rhombic system, has a hardness of 2.5 on a scale of ten, has the m.-p.  $112.8^{\circ}$  C., is not perceptibly soluble in water but dissolves in carbon disulphide (41 parts : 100 at  $18^{\circ}$ ), has the b.-p.  $444.7^{\circ}$  C., the sp. gr. 2, and is a very poor conductor.

Slight variations from the standard properties of the substance usually indicate the presence of an impurity homogeneously incorporated. The precise ways in which properties are affected in such cases will be noted under solutions.

The "substance" will be seen to be of an *abstract* nature. It is a conception built up by selecting (or abstracting) the properties common to all specimens. Hence we classified chemistry as an abstract-concrete science (p. 2). The *bodies* under observation are *concrete*, the *classification of the results* is under conceptions of an abstract nature like this one.

**Attributes and Conditions.** — There are other qualities which a body may possess that we are likely to confuse with the specific properties. Thus, the weight of a piece of sulphur is not a property

of sulphur. A hundred pieces of as many different substances might all have the same weight, so that a particular weight (say 2 grams) is not a property of any one species of matter. **Weight, dimensions, and volume are attributes of a body.** They have different values for different bodies, even when those bodies are all composed of the same substance. The attributes are physical in nature. They are of great importance in chemistry, however, because they afford the only means we have of measuring quantities of matter.

There are still other qualities which a body (or specimen of matter) may possess. It has, for example, a certain **temperature, pressure** (state of compression), **motion**, kind of **illumination**, or **electric charge**, and it may be **in solution** in some liquid. A body may change in temperature, pressure, or state of electrification, or it may be dissolved in water, or be recovered by evaporation of the liquid, and yet be the same specimen. A hundred specimens of as many different substances may all have the same temperature—this is not a specific property. These are spoken of as **conditions**. They are physical conditions. In chemistry, conditions are often altered in order to bring about, or to stop chemical change; or to modify the speed with which it takes place. Thus we heated the lead (raised its temperature) in order to hasten the process of rusting. If a substance, or mixture, is capable of undergoing chemical change, then the change is always hastened by raising the temperature, and is always delayed or prevented by lowering the temperature. Similarly, changing the pressure of gas, or dissolving a substance in some liquid, frequently hastens or delays a chemical change in which the substance takes part. Again, silver chloride decomposed when illuminated, but not in the dark. The proper physical conditions are, therefore, considered in connection with every chemical operation. **Conditions are used to produce, modify, or control chemical change.**

Since the density of a substance changes with the temperature, we must define the density as the weight of 1 c.c. at 4° C., or some other *temperature*. We must mention also the *pressure*, particularly in the case of gases, and even in the cases of liquids and solids if it differs from one atmosphere. Again, the melting-point is the *temperature* at which the substance melts at one atmosphere *pressure*. Thus, the **conditions are used also in defining the specific physical properties.**

When the word "properties" is used in speaking of a substance, we always refer to the specific properties only, for a substance is by definition the bearer of nothing but constant, that is, unchangeable qualities. The weight and volume,



the temperature and pressure, are variable, and they do not enter into the conception of the substance. This distinction sets the abstract nature of the "substance" in high relief.

**Methods of Work and Observation in Chemistry.**— It is not the end of chemical work to make generalizations or laws (pp. 6, 11, etc.), or conceptions, like those dealt with in the preceding paragraph. These are simply the *means* by the help of which chemical work, whether it be investigation, commercial analysis, or manufacturing, may be carried on more systematically. Together they constitute our system for classifying the facts with a view to ready reference. The sample experiments (pp. 12–21), if reexamined, will show that we there employed most of the categories of our classification which have so far been described.

Thus, in the experiment with iron and sulphur (p. 14), it was first our object to find out whether the bodies had interacted chemically on being mixed. To do this we noted the *specific properties* (p. 3\*) of the substances, separately. Using these properties, we were able to **identify** the same substances in the mixture, and in this we found no substance with new properties. Part dissolved in carbon disulphide and reappeared after evaporation of the solvent as yellow, rhombic crystals, and the rest was all magnetic. In this connection we purposely omitted all mention of the quantity and temperature, because attributes (p. 41) like the former and conditions (p. 41) like the latter do not characterize substances (since they vary with each specimen), and cannot be used for identification. Coincidence in two or three specific properties is generally sufficient to establish identity.

Most of the properties cannot be recognized readily in *mixtures*, as a moment's thought will show. The general color and the specific gravity of a mixture, containing unknown substances in unknown proportions, for example, tell us little about the corresponding properties of the components. Now, there are few pure substances in nature or in the products of experiment, and many mixtures. Hence, **separation** of the components of a mixture usually of necessity precedes the process of identification just referred to. Thus, we first removed the sulphur by dissolving it and then recovered it by evaporation of the solvent, the *boiling-point* of the carbon disulphide (46°) being much lower than that of the sulphur (445°) and its vapor pressure, by virtue of which it evaporated at the temperature

\* See footnote on p. 14.

of the room, being therefore relatively high. We secured the iron because of its *insolubility*. Those specific properties which can be used for separating mixtures, as well as for identification, are therefore the most important of all. They are the melting-point, solubility, boiling-point, specific gravity, and magnetic qualities, the last being applicable almost exclusively to iron, however.

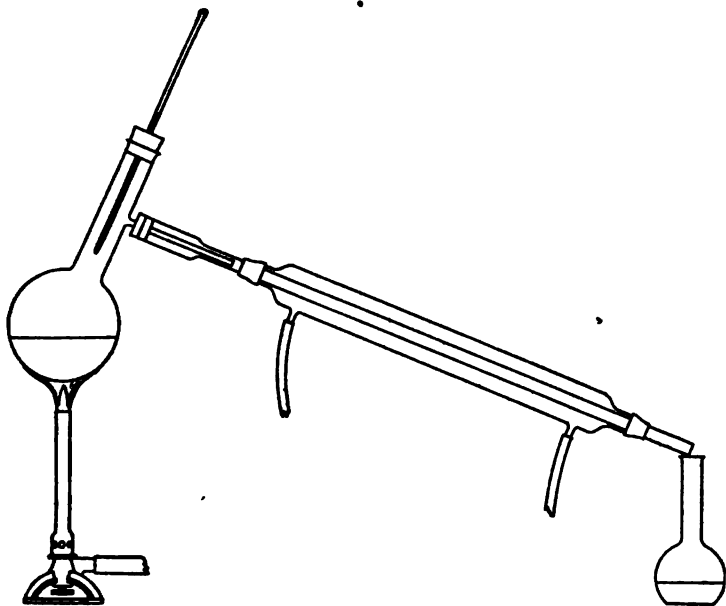


FIG. 20.

In connection with this investigation we employed several of the common methods of **manipulation** used by the chemist. These methods are derived from the conceptions described in last paragraph. Thus we **treated the mixture with a solvent** (Fig. 9), on the assumption that if it was heterogeneous (p. 7) the components would each behave as if alone present. We then **filtered**, a method invented for dealing with a heterogeneous mixture consisting of a solid and a liquid. **Decantation** is often used in such cases, when the solid is specifically much heavier than the solvent and settles readily. We allowed the carbon disulphide to **evaporate** spontaneously, and this is our favorite method of dealing with a mixture which is homogeneous, and therefore would run through a filter as a whole without suffering

separation. When the liquid has a higher boiling-point than 50–60° C., as water has, we use heat from a steam-bath or Bunsen flame to promote the evaporation. In evaporation we allow the vapor of the liquid to escape, because it is the less volatile, dissolved body that we wish to examine. When we desire, on the contrary, to examine the liquid, the vapor must be condensed. This method, which we have not yet had occasion formally (see, Exercise 5) to employ, is called **distillation** (Fig. 20). The jacket round the long tube is filled with a stream of cold water, which, on account of its high specific heat, quickly cools and condenses the vapor. The resulting liquid is caught in a flask.

These methods may be adapted to the investigation of any similar problem. Thus, gunpowder is made by the intimate mixing of sulphur, charcoal, and saltpeter (potassium nitrate). If no chemical interaction whatever has occurred, a sample will be wholly separable into these components. If a partial change has taken place, a certain amount of material with different properties will be discovered in the mixture. If the change has been complete, no portion of the original substances will be found. We must first study the specific properties of each of the ingredients separately, in order that a plan of separation may be devised, and that we may have a basis for comparison with the products of the separation.

It should be noted that our methods of investigating the products of nature and of the laboratory are purposely limited so as not to separate chemically combined, but only physically mixed forms of matter. After a physical individual has been isolated, and even then only if it has new properties, and is not at once recognized as a known substance, we next proceed to separate it into its chemical constituents so as to learn which constituents it contains and in what relative proportions by weight.

The experiments with mercuric oxide and with silver nitrate simply rang the changes on the same conceptions, and repeated the same manipulations. In every case the specific properties — color, crystalline form, volatility, solubility, and so forth — by which separation and recognition were effected will be found to have been mentioned. When we heat the mercuric oxide (p. 17),\* it is resolved into its constituents. We selected the experiment because the conditions are such that separation of the products from each other and from the original material occurs spontaneously, without further manipulation. The separation depends here on the boiling-points

\* See footnote on p. 14.

of the materials. That of oxygen is very low ( $-183^{\circ}\text{C.}$ ); so that, being a gas even at ordinary temperatures, it comes off. That of mercury is much higher ( $357^{\circ}\text{C.}$ ), but the heat produced by the flame ( $1000^{\circ}$ – $1200^{\circ}\text{C.}$  in the bottom of the test-tube) is more than sufficient to vaporize this product also. The speedy condensation on the cooler part of the tube, causing *separation* of the two products, is due to the wide *difference in boiling-points*. The part of the mercuric oxide which is still unchanged, on the other hand, is entirely involatile even at  $1200^{\circ}\text{C.}$ ; so that it does not mingle with the vaporized products at all.

In the action of silver nitrate on sodium chloride (p. 19), it was solubility that furnished the means of separating the products. The silver chloride is practically insoluble in water, while sodium nitrate is very soluble. To recover the latter, the boiling-points were then considered, and the more easily vaporized water was driven off.

When, following the latter experiment, the silver chloride was exposed to light, resolution into silver and chlorine took place. The products became separated spatially at once, because chlorine is a gas (substance of low b.-p.) and silver is a solid (usually a substance of high b.-p.).

**Fact and Law.** — If the preceding pages be reexamined, it will be seen that a number of **facts** are mentioned in them. We begin the organization of knowledge according to the scientific method by trying to determine the facts. Thus, we find some specimens of iron are variously colored, and some are brittle. Examination shows, however, that the former peculiarities are due to paint, for example, and the latter to the presence of carbon and other foreign materials in the iron (cast iron). Finally, we ascertain the facts that iron itself is silver-white and tough.

Facts are the ultimate units of the structure of a science. Thus, a single isolated observation, no matter how accurately made, does not furnish us with the sort of fact that can receive a permanent place in our collection. It is only after much research and thought that we can ascertain which are the fixed elements in the variety of experience in any line, and so determine what are the facts, in the sense in which we have used the term.

Putting together statements or **laws** like those appearing in heavy type above (pp. 11, 17, 18), is the second step. We examine facts of a like kind, or pertaining to like phenomena, to see whether any general statement can be made that will cover some feature

common to the whole of them. For example, after settling the intrinsic properties of several substances, and then determining the facts about the way in which these properties are affected under certain circumstances, we decide that, when one substance gives two entirely different substances, or one of the other varieties of change (p. 21) occurs, the cases in which this takes place shall constitute a distinct class, and we call them cases of chemical change. The statement which in a few words or phrases sums up those features of all the phenomena of like kind which are constant, is called a **generalization**, or a **law**, or a **principle** of the science. A **generalization** or **law** in chemistry, therefore, is a **brief statement describing some general fact or constant mode of behavior**.

We must remember that laws are only true so long as no facts in conflict with them are known. There are no laws in nature. Nature presents materials and phenomena as she pleases. The laws are parts of science, which is made by man (p. 1), and is a description of natural facts as man knows them. As we shall see (p. 54), at least one undoubted exception to the law of constant proportion has recently (1914) been discovered, and other exceptions to this law will undoubtedly turn up. A law is true only at the date of its formulation by one chemist and its acceptance by other chemists, and only so long as no facts to the contrary become known.

Of course, the same set of facts may be viewed in many ways. Picking out the relationships which are most comprehensive and, at the same time, are best fitted to form part of still broader generalizations, or to take their places alongside of equally broad ones, requires the highest ability. The most important laws, like that describing the behavior of gases when compressed (Boyle's law), are usually connected with the names of the men by whom the relationships were discovered and the generalizations formulated.

The word "formulate," as applied to a law, is preferable to the word, "discover." The latter is ambiguous and suggests that the law existed before it was found. Even the relation which it puts into words, did not, properly speaking, exist, because relations are picked out of a complex by the mind, and the particular relation selected is a property of the mind and not of the constituents of the complex itself.

The reader must beware of the misconception that a law *enforces* behavior in accordance with its tenor. The mere *statement* that every piece of matter attracts every other, cannot compel a stone to fall; nor can the mode of behavior of one falling stone persuade any other to do likewise. The law is simply a record of what is invariably observed to happen.

It is, therefore, also very misleading if we permit ourselves to say that Boyle's law "acts" so as to "cause" gases to behave in a certain way, or that the law

"operates" to "produce" a certain behavior, or that other behavior is "impossible" to the gas, or that the law of cohesion "intervenes" when the gas is under low pressure, and causes its behavior to "diverge from that required" by Boyle's law, or to say that a gas "disobeys" Boyle's law. In scientific discussions, such figures of speech are alone permissible as throw light on the subject. Phrases like the above, common as their use is, have been selected apparently with a view to introducing a maximum of distortion and obscurity. It is the gas that "acts" and gives rise to the making of Boyle's law, and the latter is only an epitome of the way it acts. The "laws" of nature are not unchanging, although we are often told that they are. It is the *behavior* in nature that is unchanging. The laws which attempt to describe this behavior are not natural laws, they are man made. They are continually amended, that they may more closely describe additional facts disclosed by research. Behavior divergent from the "laws of nature" is not only possible, but is constantly being observed. Such divergencies furnish, in fact, the commonest starting points for fresh investigation. Thus Boyle's law was amended by van der Waals (p. 165), and the law of octaves (*q.v.*) was greatly modified by Mendelejeff. It is not the gas which "diverges" from our statement or "disobeys" our law, but our statement which is proved by the behavior of the gas to be inaccurate. Our procedure, in such cases, is always more logical than our language, for we never attempt to cure the gas of its error, but always the law itself by suitable modification in its phraseology.

**Physics in Chemistry.** — It will be seen that one cannot accomplish anything in chemistry without acquiring and using some knowledge of physics. We measure quantities by means of the physical attributes, weight and volume. We produce chemical change by arranging the physical conditions, for example, by mixing, heating, or using an electric current. Physical means are the only means we possess for producing, stopping, or modifying chemical changes. Again, we ascertain whether a chemical change has taken place or not by observing the physical properties of the materials before and after the experiment. Thus, we noted that the red, powdery oxide of mercury, when heated, gave a liquid metal and a gas. All the phenomena of chemistry are physical. A phenomenon (Gk. *phaino*, to show) is literally something that is *seen*, or more generally, something that affects any of the senses. Observing physical phenomena is, therefore, our sole means of studying chemical changes. Chemical work is therefore entirely dependent upon the skilful use of physical agencies, and the close observation of physical phenomena for its success.

It is only the inference, following the experiment and the observation, that is strictly chemical. If one substance gives two different substances, or if two substances give one different substance, for

example, we infer that a chemical change has occurred. We then try to recognize the substances by their properties and name them.

Changes like that of ice into water, or of water into steam, and *vice versa*, are not regarded as chemical changes. These are called **changes of the state of aggregation**. The solid, liquid, and gaseous forms are different states of the same substance. The very language we use bears testimony to the universal acceptance of the view that change of state does not constitute a fundamental alteration. Thus, we have solid *lead* and molten *lead*, *air* (the gas) and liquid *air*. In the case of water alone has it been found convenient to distinguish the three forms, ice, water, and steam, by separate names.

### ***Attempts to Distinguish between Physics and Chemistry.***—

If the reader has studied elementary chemistry before, he must beware of certain misconceptions which he may have formed in regard to the relation of physics to chemistry. For several reasons, we have omitted most of the usual material employed in discussing the difference between chemistry and physics. To discuss the *difference* between two things, when the reader does not yet know anything about one of them (chemistry), and sometimes knows little or nothing about the other, must necessarily be futile. Then, too, the alleged difference between physical and chemical phenomena, as phenomena, does not exist. Heating a platinum wire and allowing it to cool, heating mercuric oxide and decomposing it, and an animal walking, when regarded as phenomena (appeals to the senses) are all physical. The phenomena presented in chemical change, in the structure of plants and animals, in geological formations, and in pure physics are all physical. After we have assigned certain groups of such phenomena to other sciences, what is left belongs to physics as such. But physics still has to be employed in explaining how the limbs of an animal work, how strata are deposited, and how the mercury and the oxygen are separated, and how each is recognized in the practical study of chemistry. We cannot omit physics because it is needed at every turn. Chemistry deals with the interpretation of certain classes of physical phenomena, geology with other classes, and so forth.

Some of the current distinctions between chemical and purely physical phenomena deserve notice. Some physical changes, like the boiling of water and the condensation of the steam, are easily reversible. But no one ever saw a piece of broken glass restored to its original condition. Many toys are broken, and few mended. In fact, some physical changes are easily reversible, and others are not. We shall see later that many chemical changes are also easily reversible, although many are not. There is no distinction along this line. Again, in chemical change, all the physical properties are altered. But, when water is converted into steam or ice, all the physical properties are different. Change in all physical properties occurs in physics also. Still again, the change from iron to rust is abrupt or sharp, while the changes in the properties of iron as it is gradually raised to higher and higher temperatures are gradual. But,

when the iron melts, or the water is changed into steam, the change is very sharp. On the other hand, when water is heated from  $0^{\circ}$  to  $100^{\circ}$ , chemical changes from  $(\text{H}_2\text{O})_3$  to  $(\text{H}_2\text{O})_2$  and  $\text{H}_2\text{O}$  occur and, when ammonium chloride vapor is heated, more  $\text{NH}_3 + \text{HCl}$  is formed and less  $\text{NH}_4\text{Cl}$  remains, yet no sharp change in properties is noticeable. The absence of abrupt change is due to the fact that the substances in the water and the gases in the vapor are *completely miscible with one another*, so that only gradual change can be noticed. On the other hand, rust and iron, or water and steam, are not miscible, and so two phases are produced. Hence, the change (physical or chemical) is sharp if a new phase is produced, but gradual if the products are miscible with the original substances. Finally, it is sometimes said that physical changes are produced by physical or mechanical means, and chemical changes by chemical means. In point of fact chemical changes are produced by mixing substances, or by heating (producing more violent motion of the molecules), or by using a current of electricity (driving a stream of electrons into the solution), or by other physical and mechanical means, and no other means exist. Practical chemistry consists, therefore, in using physical means to produce and to control chemical change, and to separate and examine the results. Hence, while studying real chemistry, one is bound to use, and to learn much about, practical physics.

**Where Physics and Chemistry Meet.** — In the completeness of the transformation, and in the fact that only one original substance and one product are required, the physical changes of the nature of melting a solid and vaporizing a liquid resemble the fifth variety of chemical change. Where, then, is the line between chemistry and physics to be drawn? It is in this fifth group only that the difficulty is encountered. All agree that warm solid phosphorus is chemically identical with cold phosphorus. Nearly all scientific men at present assign the study of the melting and the vaporization of phosphorus and other substances to physics. Some chemists consider the solution of phosphorus in carbon disulfide or some other solvent (it is practically insoluble in water), although the material is recovered unchanged by evaporation of the liquid, as a chemical change. But the great majority regard this as physical also. If not chemically different, the solid, liquid, gaseous, and dissolved forms of a substance must be classed as mere physical states of aggregation. On the other hand, red phosphorus is held by most chemists to be chemically different from yellow phosphorus. Many kinds of matter show as much variety in form as phosphorus, and some show more.

In solving an ordinary puzzle, we work knowing that some simple solution exists. When studying nature, we are saved much embarrassment by remembering that, in cases like this, we are not seeking for a clear-cut distinction of whose existence we are assured in advance. Nature is under no obligation to furnish easily classifiable facts at all. The limitations of our minds compel us to classify as far as we are able to do so. On this plan alone can we master the infinity of detail. But the resulting system exists in our own minds, where it originated, and not in nature. In the present instance, we are seeking, as always, to make a



distinction for our own convenience. But, at present, the effort to make a final distinction that can be used consistently causes more inconvenience than the alternative of letting the matter rest. The history of previous experiences leads us to hope that, with fuller knowledge, we shall be able, sooner or later, to construct a system of classification even for this obscure region. After the distinction has been made and accepted by chemists, and not till then, will it be possible to explain it to students.

**Summary.** — In this chapter we have added considerably to our conception of the scope of chemistry (*cf.* pp. 13, 26). Although our survey is by no means yet complete, we may condense our results as follows:

Chemistry deals, not only with the changes in composition and constitution which substances undergo, but also with the transformations of energy which accompany them. To convert the isolated facts into a science we classify related parts under laws, such as that of conservation of energy (p. 32), and under conceptions, such as those of internal energy (p. 34), and chemical activity (p. 37). We also distinguish between specific physical properties, attributes and conditions (pp. 40–41). In the following paragraphs we have indicated briefly the use to which these conceptions and this classification are put. Finally, we have discussed the meaning of terms like cause, fact, and law, and the relation of physics to chemistry.

Chemical laboratory work consists largely in the separation, recognition, and description of substances. The importance, especially, of thorough familiarity with specific properties and the influence of conditions (for example, temperature) to these ends is shown by the examples (pp. 42–45). The system of classification as a whole is part of the everyday mode of thought of the chemist, for thought consists largely in comparing and contrasting, and our system of classification furnishes the plan of this so far as chemistry is concerned. Learning chemistry consists, therefore, in large part in learning this classification and becoming habituated to its use.

The influence of conditions has as yet been barely touched. It will be dealt with more explicitly as occasion offers. The attribute of quantity, which has already received some attention (p. 13), will form the basis of discussion in the next chapter.

**Exercises.** — 1. What is the original form of energy used in, (a) a hydro-electric plant, (b) an automobile, (c) a watch, (d) a clock with weights?

2. From what form of energy comes, (a) the heat of a burning candle, (b) the heat in an electric light, (c) the electricity of a battery?

3. Describe, (a) a red-hot rod of iron, 10 cm. long by 1 cm. diameter, weighing 58.5 g., (b) a solution of 5 g. of sulphur in 20 c.c. of carbon disulphide at 18° C. In doing so, divide the description into attributes, conditions, and properties.

4. Color, volume, melting-point, density, temperature, weight, crystalline form, boiling-point, pressure. In respect to which of these qualities will, (a) one substance differ from another, (b) one specimen of the same substance differ from another, (c) one specimen of the same substance differ at different times? Give the technical names and uses of the sets of qualities which fall under *a*, *b*, and *c*, respectively.

5. What properties are essential in order that two substances may be separated by, (a) evaporation, (b) filtration, (c) distillation?

6. What is the cause, (a) of the precipitation of silver chloride (p. 19), (b) of the union of iron and sulphur (p. 16)?

## CHAPTER III

### COMBINING PROPORTIONS BY WEIGHT

If we now return to the illustrations of chemical phenomena which we have been studying (pp. 14-21), we shall find a new question arising naturally out of them. This is, whether the *mass* of the materials is altered, as are the other attributes, in these chemical changes.

**Conservation of Mass: Fourth Characteristic of Chemical Change.**—The most painstaking chemical work seems to show that, if all the substances concerned in the chemical change are weighed before and after the change, there is no evidence of any alteration in the *quantity of matter*. The two weights, representing the sums of the constituents and of the products respectively, are, indeed, never absolutely identical, but the more careful the work and the more delicate the instrument used in weighing, the more nearly do the values approach identity. We are able to state, therefore, as a law of all chemical phenomena, that: **The mass of a system is not affected by any chemical change within the system.**

This statement simply means that the great law of the conservation of mass holds true in chemistry as it does in physics. Chemical changes, thoroughgoing as they are in respect to all other qualities, do not affect the mass; an element carries with it its weight, entirely unchanged, through the most complicated chemical transformations.

A law, as we have seen (p. 45), is a condensed statement describing some constant mode of behavior. It is simply a summary of our experience. As such, it is subject to modification when a fact is discovered with which it conflicts. Thus, it is perfectly possible that we may yet find cases of demonstrable changes in weight accompanying other physical or chemical changes in a limited system. Indeed, it has more than once been alleged that such changes have been observed. It used to be a law that the earth was flat. It is now more correct to say that a limited area of perfectly level ground is *very nearly* flat.

It will be observed that the phrasing of the above law carefully limits its scope to amounts of matter such as are dealt with in laboratory experience. We have no evidence on which to make any statements about the mass of matter in more extensive chemical changes. A common form of the law, to the effect that "the mass of matter in the universe is unchangeable in amount," is not a law at

all, in the only sense in which the word is used in science. It is a statement in regard to supposed facts which are almost entirely beyond our experience. It is, therefore, a proposition of a transcendental (that is, transcending experience) nature, and has its proper place in metaphysics. Astronomical observation, it is true, has as yet furnished no evidence of changes in the mass of our own or other celestial systems. But, absence of evidence to the contrary, especially considering the relatively limited scope of our knowledge, both in respect to space and time, is far from being proof of the correctness of the proposition.

Superficial observation, as of a growing tree, might seem to give evidence of the very opposite of conservation of matter. But here the carbon dioxide gas in the air, the most important source of nourishment for plants, is overlooked. Similarly the gradual disappearance of a candle by combustion seems to illustrate the destruction of matter. But if we insert sticks of sodium hydroxide in a U-tube (Fig. 21) to catch the gases which rise through the flame, we find that the gases weigh even more than the part of the candle which



FIG. 21.

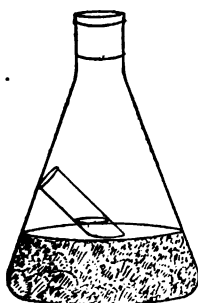


FIG. 22.

has been sacrificed in making them. When we take account of the weight of the oxygen obtained from the air which sustains the combustion, we find that there is really neither loss nor gain in weight. If we carry out chemical changes in closed vessels (Fig. 22), which permit neither escape nor access of material, we find that the weight does not alter.

One way of stating the difference between chemistry and physics is to say that changes in which both the mass and the identity of the substance are conserved belong to the latter, while those in which the mass alone is conserved belong to chemistry.

**The Law of Definite Proportions: Fifth Characteristic of Chemical Change.**—In making a chemical compound, may we use varying proportions of the constituents? The controversy between Berthollet and Proust, in which the former supported the affirmative and the latter the negative side of this question, was one of the chief features of the chemical history of the early part of the nineteenth century. The ways of forming or decomposing a compound, or of carrying out a more complex chemical change, may be varied indefinitely. The apparatus, the mode of experiment, and the proportions of the materials, may be altered at our will. But, in spite of an enormous amount of careful work, no case of variation in the proportion of the constituents *actually used* or *produced* in a given chemical action has come to light. If too much of one constituent, for example, is taken, a part simply remains unchanged. A higher temperature may hasten the chemical action, but it does not affect the quantitative composition of the products, provided the resulting substances are of the same nature. It was the work of Stas (1860–65) which settled the question, by proving that even slight variations cannot be detected, and disposed of Berthollet's objections. It is, therefore, a characteristic of chemical phenomena that: **In every sample of each compound substance formed or decomposed, the proportion by weight of the constituents is always the same.** This statement of fact is known as the **law of definite, or of constant proportions.** When the composition of a substance seems to be variable, it is always found on closer examination that mechanical mixtures of some kind were being mistaken for pure substances.

Another form of statement, which is a corollary of this one, and is applicable more directly to complex chemical actions, is: **The ratio by weight of any one of the factors or products of a chemical change to any other is constant.**

One exception to this law has been discovered. Ordinary lead chloride contains lead and chlorine in the proportion  $207.2 : 2 \times 35.46$ . Richards, of Harvard, however, has found that the lead contained in uranium ores gives a chloride in which the proportion of lead is from 206.4 to 206.8 to the same weight of chlorine. Honigschmidt and Horowitz found lead from the same general source to give in some cases proportions as low as 206.05 and 206.06, yet this lead gave the same spectrum as ordinary lead. Richards found this lead to have a density slightly lower (11.288) than that of ordinary lead (11.337). Again, Soddy found that lead extracted from thorium ores gave a chloride containing a proportion of lead *higher* than the

ordinary ore, namely,  $208.4 : 2 \times 35.46$ . There thus appear to be three chlorides of lead, having, so far as we know, the same properties, and *being therefore the same substance*, yet differing in composition. This illustrates the fact that a law is true only until facts at variance with it are encountered. This law was absolutely true up to 1914, but is now true of all compounds with the exception of those of lead extracted from the ores of uranium and thorium. Still other exceptions will undoubtedly be discovered very soon.

**The Measurement of Combining Proportions.** — The most *exact* measurement of the proportions in which the elements combine to form compounds involves manipulations too elaborate to be gone into here. Operations of the same nature are described in works on quantitative analysis. One or two brief statements, diagrammatic rather than accurate, will show the principles, however.

If we take a weighed quantity of iron in a test-tube and heat it with more than enough sulphur (an *excess* of sulphur), we get free sulphur along with the ferrous sulphide (p. 16), and no free iron survives. We may remove the free sulphur by washing the solid with carbon disulphide. The difference between the weights of ferrous sulphide and iron gives the amount of sulphur combined with the known quantity of the latter.

As an example of the study of rusting, we may weigh a small amount of copper in the form of powder in a porcelain boat and pass oxygen over the heated metal (Fig. 23). The formation of cupric oxide takes place rapidly. If we limit the oxygen, part of the copper may remain unaltered; if we use it freely, the excess will pass on unchanged. A given weight of copper cannot be induced to take up more than a certain amount of oxygen, and use of a less amount simply limits the amount of copper transformed into oxide. The original weight of the copper, and the increase in weight, representing oxygen, give us the data for determining the composition of cupric oxide. The data furnished by one rough lecture-experiment, for example, were as follows:

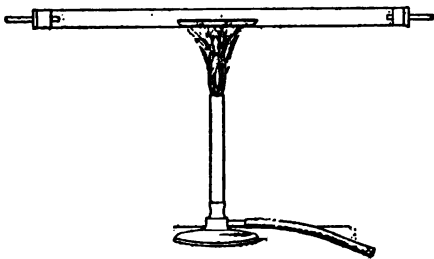


FIG. 23.

Weight of boat + copper.....	4.278 g.
Weight of boat empty.....	3.428 g.
Difference = <b>weight of copper</b> .....	<u>0.850 g.</u>
Weight after addition of oxygen.....	4.488 g.
Weight without oxygen.....	4.278 g.
Difference = <b>weight of oxygen</b> .....	<u>0.210 g.</u>

The proportion of copper to oxygen, so far as this one measurement goes, is therefore 85 : 21.

The results of quantitative experiments are usually recorded in the form of parts in one hundred. To find the percentage of each constituent, we observe that the proportion of copper is 85: 85+21, or  $\frac{85}{106}$  of the whole. That of the oxygen is  $\frac{21}{106}$  of the whole. Thus the percentages are:

$$\begin{array}{llll} \text{Copper,} & 106 : 85 :: 100 : x & x = 80.2 \\ \text{Oxygen,} & 106 : 21 :: 100 : x' & x' = 19.8 \end{array}$$

Naturally, the mean of the results of a number of more carefully managed experiments will be nearer the true proportion. The percentages at present accepted as most accurate are 79.9 and 20.1.

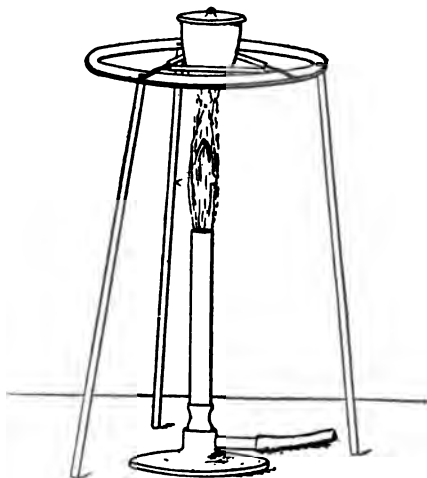


FIG. 24.

In the case of mercuric oxide, we may decompose a known weight of the oxide (p. 17) and afterwards weigh the mercury and ascertain the oxygen by difference.

Finally, a strip of the metal magnesium may be set on fire in the air. It gives out a dazzling white light in burning, and on this account the powdered metal is used in making flash-light powder for photography. The product is magnesium oxide, a white substance,

which partly rises as a dense smoke and partly falls on the ground. In a loosely closed porcelain vessel (Fig. 24) the metal may be burned slowly, with the help of the heat from a small flame, and the oxide may be retained. The weight of magnesium ribbon taken

and the increase in weight due to oxygen give the data for calculating the proportions of the constituents.

The following figures show the results of some experiments like these, and represent the percentage composition of the products. Only two places of decimals are given in each case, the numbers following the second decimal being omitted, and hence the total, in one instance, appears to be only 99.99. The numbers in parenthesis will be explained presently:

(1) **Cupric oxide**

Copper	79.9	$\left[\frac{31.8}{8}\right]$
Oxygen	20.1	

(2) **Mercuric oxide**

Mercury	92.61	$\left[\frac{100.3}{8}\right]$
Oxygen	7.39	

(3) **Water**

Hydrogen	11.18	$\left[\frac{1.008}{8}\right]$
Oxygen	88.81	

(4) **Chlorine monoxide**

Chlorine	81.8	$\left[\frac{35.46}{8}\right]$
Oxygen	18.2	

**Combining Weights.** — The percentages in the above list represent the true proportions by weight in the various compounds, but naturally the individual numbers constituting those proportions have no chemical significance whatever. They are arbitrary values selected so that the two factors in the proportion may together make 100. Each pair represents the constant ratio which is the mean result of numerous experiments.

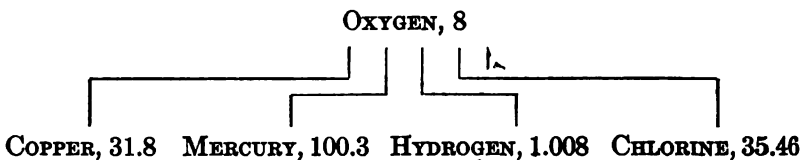
We begin the effort to reduce these numbers to order by selecting one element as our starting-point, and by taking some convenient weight of it as the basis. As we shall see, it makes *no difference* what choice we make in either respect. To avoid waste of time, we shall, therefore, use oxygen, as it is the element generally preferred by chemists for the purpose. The reason for this preference will be apparent later (see pp. 61, 66).

We should naturally be inclined to use 1 part of the element as our basis. But our later steps involve finding out what amounts of the other elements combine with this quantity, and we perceive that the amount in the case of hydrogen will be only 0.126 parts. We calculate this from (3):  $88.81 : 11.18 :: 1 : x$  ( $= 0.126$ ). If, however, we take 8 parts of oxygen, this amount of hydrogen is also increased eight times and becomes 1.008. As no element is found to combine in smaller proportions than hydrogen, we are satisfied that a scale for our numbers based on 8 parts of oxygen will not involve any values less than 1. The choice of scale is purely one of convenience.

We now proceed to calculate from the data given above the weight of each of the other four elements which combines with 8 parts of



oxygen. From (1) we calculate this weight of copper, thus,  $20.1:79.9::8:x$  ( $= 31.8$  parts of copper). Similarly we find that 8 parts of oxygen combine, in (2) with 100.3 parts of mercury, in (3) with 1.008 parts of hydrogen, and in (4) with 35.46 parts of chlorine. Oxygen unites with almost all the known elements, and these four compounds have been chosen simply as a sample group.



Now chlorine combines, not only with oxygen, but also with copper, mercury, and hydrogen, and measurement shows that *the combining proportions are represented, exactly, by the very same numbers as before*. From the two independent facts that 8 parts of oxygen combine with 31.8 parts of copper and with 35.46 parts of chlorine, we could not possibly have foretold the proportions in which copper and chlorine would combine with one another. Yet measurement shows it to be  $31.8:35.46$  precisely. In the following table the proportions in which the elements combine with chlorine are placed under the corresponding parts of the names of the compounds with chlorine:

CUPRIC CHLORIDE	MERCURIC CHLORIDE	HYDROGEN CHLORIDE
31.8 : 35.46	100.3 : 35.46	1.008 : 35.46

If additional elements had been included in the group, a combining number could have been found for each, and seeming coincidences of the same nature would have multiplied rapidly. Thus, sulphur unites with hydrogen to give hydrogen sulphide. If, to maintain the same scale, we use 1.008 parts of hydrogen in expressing the proportion, we find that the combining ratio is  $1.008:16.03$ . This result could not enable us to predict the proportion of copper to sulphur in cupric sulphide, but measurement shows it to be  $31.8:16.03$ . Again, mercury and sulphur unite in the proportion  $100.3:16.03$ .

SULPHUR, with the value 16.03, may therefore be added to the series of equivalent weights.

**Law of Multiple Proportions.** — One other remarkable fact remains to be noted. There are *two different* compounds of copper with oxygen. Cuprous oxide (*q.v.*), the one not mentioned hitherto,

is found in nature as a dark-red mineral which is entirely different from cupric oxide in physical properties. It can also be prepared in the laboratory, but not by simply passing oxygen over heated copper. Now, analysis shows that in cuprous oxide the proportion of copper combined with 8 parts of oxygen is 63.6. This new number for copper is not unrelated to the corresponding value in cupric oxide (*viz.*, 31.8), for it is *exactly twice as great*. Again mercury forms mercurous oxide (see below) as well as mercuric oxide, and in the former the proportion of oxygen to mercury is 8 : 200.6. The proportions of mercury uniting with 8 parts of oxygen are therefore 100.3 and 200.6, and no other proportions are known. Still again, 1.008 parts of hydrogen unite with 8 parts of oxygen in water and with  $2 \times 8$  parts of oxygen in hydrogen peroxide. The fact suggested by these three examples is a general one. It was discovered by Dalton (1804) and was embodied by him in a statement known as the law of multiple proportions, which ran somewhat as follows: If two elements unite in more than one proportion, forming two or more compounds, the quantities of one of the elements, which in the different compounds are united with identical amounts of the other, stand to one another in the ratio of integral numbers, which are usually small.

***The Law of Combining Weights: Sixth Characteristic.***—

The reader should now examine carefully the following table of combining proportions. It includes *all* the compounds made up of pairs of the six sample elements under consideration, so far as the existence and composition of such compounds have been determined with certainty. The substances in black type are the ones from whose composition we originally derived the combining numbers, the others illustrate the uniform recurrence of the same numbers:

<b>Cupric oxide</b> 31.8 : 8	<b>Mercuric oxide</b> 100.3 : 8	<b>Hydrogen monoxide (water)</b> 1.008 : 8
Cuprous oxide 2×31.8 : 8	Mercurous oxide 2×100.3 : 8	Hydrogen peroxide 1.008 : 2×8
<b>Cupric sulphide</b> 31.8 : 16.03	<b>Mercuric sulphide</b> 100.3 : 16.03	<b>Hydrogen sulphide</b> 1.008 : 16.03
Cuprous sulphide 2×31.8 : 16.03	Mercurous sulphide 2×100.3 : 16.03	
<b>Cupric chloride</b> 31.8 : 35.46	<b>Mercuric chloride</b> 100.3 : 35.46	<b>Hydrogen chloride</b> 1.008 : 35.46

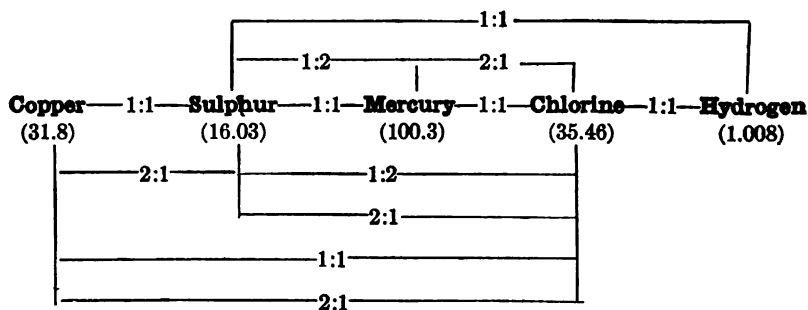
Cuprous chloride	Mercurous chloride	
$2 \times 31.8 : 35.46$	$2 \times 100.3 : 35.46$	
Sulphur dioxide	Chlorine monoxide	Sulphur monochloride
$16.03 : 2 \times 8$	$35.46 : 8$	$2 \times 16.03 : 35.46$
Sulphur trioxide	Chlorine dioxide	Sulphur tetrachloride
$16.03 : 3 \times 8$	$35.46 : 4 \times 8$	$16.03 : 2 \times 35.46$

It will be observed that the same number serves always to express the combining proportions of a given element, provided that multiplication by an integer is permitted when necessary. There are also some combinations of *three* of the same elements in one compound. But even in such cases the fundamental numbers still reappear. Thus oxygen, chlorine, and hydrogen combine in the proportions:

$$2 \times 8 : 35.46 : 1.008, \quad 6 \times 8 : 35.46 : 1.008, \quad \text{and} \quad 8 \times 8 : 35.46 : 1.008.$$

Nor is the recurrence of a fundamental number an exclusive property of the six elements we have chosen for illustration. A vast table containing every known element, and every compound of every element, if prepared in the same way as that given above (by starting with a fixed number for one element and calculating the combining proportions in all the compounds with this number as a basis), would show that every element uses an individual, fundamental number, or integral multiples of this number, in every one of its combinations. No exceptions to this rule would be found in the whole mass of data.

These relations become clearer when represented diagrammatically. Thus the five elements, omitting oxygen, give the following compounds and no others:



It will be observed that hydrogen forms stable compounds with only two of the other four elements in the series. If, however, oxygen had been included,

compounds of oxygen with all the other five would have demanded recognition. This illustrates the reason given below for the preference of oxygen as the fundamental element.

The law of combining weights may be put briefly thus: In every compound substance, the proportion by weight of each element may be expressed by a fixed number, one for each element, or by a multiple of the number by some integer (whole number). It describes what is perhaps the most striking of all the characteristics of chemical action. Clearly it does not apply to mixtures, for any irregular proportion could be used in the physical process of mixing.

It is, perhaps, hardly necessary to point out that the law of multiple proportions is simply a partial statement whose whole content is included in this far greater generalization. No one chemist succeeded in discovering this property of combining weights. The work of J. B. Richter, Dalton, and many others contributed to it.

Most of the first exact determinations of combining proportions were made by Berzelius before 1830. It should be added that, while the combining weights, with the exception of that of oxygen which is the standard, are never actually whole numbers (although they often approach such integral values), the integers used to multiply them, when they are employed to express combining proportions, are so most exactly. Even in determinations by methods of the highest refinement, the factors to be used in multiplying the combining weights are always found to diverge from whole numbers by amounts within the known errors of the method of measurement.

**Reëxamination of Combining Weights.** — If the reader will now reëxamine carefully the way in which the data were handled, the following significant facts will be noted:

1. Oxygen was made the starting-point of the system and the value 8 was assigned to its combining weight.\* Had a different value been used, all the numbers would have been different. But the change would have affected all the numbers in the same proportion

\* Oxygen was chosen as the basis of the system because the exact determinations of the combining weights of most of the elements have actually been made by direct union with oxygen or with the help of but one intermediate step. If the question had been one of mathematics, hydrogen, the element with the lowest combining proportions, would have furnished the basis and unit of the scale. But the question was the practical one of getting the most accurate measurements for the relative magnitudes of the numbers, so oxygen was chosen instead. Nevertheless, the value 8 was selected in order that the advantage of having a mathematical unit, or something close to it, in the combining weight of hydrogen, might be retained also.

and so only the *scale* of the numbers would have been changed. An individual combining number, one for each element, would have still recurred wherever the element itself appeared.

2. Even use of another element as the initial one would not have prevented the discovery of the law. Thus with hydrogen as the initial element, and the value 1.008, no change whatever would have been noted. With a different value for hydrogen, a change of scale in all the numbers would have followed, but individual combining weights would have appeared as before.

3. Finally, if cuprous oxide had been used instead of cupric oxide for the first proportion, the value found for copper would have changed to 63.6, while the other numbers would have remained unaffected. But this number would serve as the combining weight of copper just as well as 31.8, for the composition of cupric oxide can be expressed by the proportion  $63.6 : 2 \times 8$  as well as by  $31.8 : 8$ , and that of cupric sulphide by  $63.6 : 2 \times 16.03$  as well as by  $31.8 : 16.03$ . An important conclusion therefore follows from these considerations, and we shall have occasion to use it presently, namely, that any one or more of the equivalent weights (with scale oxygen = 8) may be separately multiplied by an integer without its usefulness as a member of the series being at all impaired.

The importance of the fact described in the law of combining weights cannot be emphasized too strongly. Without this fact, the remembering of the compositions of chemical substances, necessary as it is to the chemist, would have been completely beyond the power of any ordinary memory. With it, the task becomes comparatively simple. It is only necessary to decide on the best system of values for the combining weights, and then, *regarding the value of this for each element as the unit of weight for that element*, to express the proportions of the element in every compound by the proper multiples. Thus, given a list of the combining weights, one for each element, only the small integral multiples have to be kept in mind in connection with each compound.

The reader will require a little time, however, before he becomes accustomed to the use, not of a single unit of weight, but of a different one for each element. Chemistry is the only science in which the physical unit of weight, which is the same for all materials, is not employed for every purpose. The physical manipulations of the chemist are carried out with the use of physical units, but the chemical results are expressed in terms of individual unit quantities of the several elements, the combining weights.

The individual units actually used for each element are not in all cases identical with those we have given. The final values will be discussed in the next two sections.

**Equivalent Weights.** — The phrase “combining weights” is a general one, referring to any values that can be employed in expressing the proportions by weight used in combining, thus, for oxygen, the values 8, 16, 24, or 32, or any other multiple of 8 would serve the purpose. Not only so, but we could arbitrarily assign any number we chose to oxygen, such as 3 or 3.14159, and call it the combining weight, provided we changed the quantities of other elements uniting with oxygen correspondingly. In other words, combining weights have no established values in chemistry. The term is, therefore, suited for use in the definition of the law of combining weights stated above, for in that law no particular scale, or way of fixing values for the numbers, is either given or required. Two other terms, namely, equivalent weights (below), and atomic weights (next section), however, do refer to a fixed scale and to a definite numerical value for each element.

The equivalent weight of each element is that weight which combines with 8 parts of oxygen or 1.008 parts of hydrogen. The equivalent weights of the different elements (*e.g.*, copper 31.8, mercury 100.3, chlorine 35.46, etc.) are so designated, because they are equivalent to the extent that they combine with equal amounts of oxygen (or of hydrogen). These numbers are frequently used in chemical work.

**Atomic Weights.** — The chemist frequently uses the idea of equivalents and the values (p. 60) we have given them. But far more often he employs a slightly differing set of numbers, which he calls **atomic weights**. The following list shows the elements whose equivalents we have been discussing, along with one or two others, added by way of furnishing a fair sample, and gives both sets of weights for the purpose of comparison:

ELEMENT.	EQUIVALENT WEIGHT.	ATOMIC WEIGHT.	ELEMENT.	EQUIVALENT WEIGHT.	ATOMIC WEIGHT.
Oxygen . . .	8	16	Iron . . . .	27.92	55.84
Copper . . .	31.8	63.6	Magnesium . .	12.16	24.32
Sulphur . . .	16.03	32.06	Carbon . . .	3.00	12.00
Mercury . . .	100.3	200.6	Aluminium . .	9.03	27.1
Chlorine . . .	35.46	35.46	Sodium . . .	23.00	23.00
Hydrogen . .	1.008	1.008	Bromine . . .	79.92	79.92

It will be seen that some equivalents have been multiplied by two, the first four and those of iron and magnesium, for example; some have been multiplied by three, like that of aluminium; some by four, like that of carbon; and some remain unchanged, like those of chlorine, hydrogen, sodium, and bromine.

**Explanation of the Law of Combining Weights: Atoms and Molecules.** — To explain the law of combining weights it was found necessary to use the third kind of explanation (p. 11), namely, the making of an hypothesis. The details of *how* two substances combine cannot be seen, so chemists had to *imagine* some details which would account for the possession of an individual unit weight by each element. If oxygen, for example, is *composed of minute, invisible particles*, which are *all alike in weight*, and hydrogen, sulphur, and the other elements are of the same nature, except that *the weight of the particle of each kind of element is different*, we have the basis of an explanation. We have to suppose, further, that, when elements combine, *the individual particles adhere in pairs or groups, as wholes, and are never broken*. In this way the particle of each variety of elementary matter will have a definite, unchangeable weight, which will be one of its fixed properties. If the relative weights of the *particles* of oxygen, copper, and hydrogen are in the proportion of the numbers in the table, namely, 16 : 63.6 : 1.008, the whole situation becomes clear. Chemical union must consist, in detail, in the union of the particles of the elements to form the particles of the compound. For each particle of cupric oxide (p. 57) the proportion 31.8 : 8, or one particle of copper (63.6) to one particle of oxygen (16), is required.

For each particle of water, where the proportion of oxygen to hydrogen is 16 : 2.016 (or 8 : 1.008), evidently one particle of oxygen and *two* particles of hydrogen are necessary. Varying, intermediate proportions are impossible, because the particles of the elements are permanent, are never broken, and combine as wholes, and in a uniform way through the mass. The only possible variation would be to take different relative numbers of the particles — for example, two of oxygen to two of hydrogen ( $2 \times 16 : 2 \times 1.008$ ). But this product would have a different composition from water, and would not be water. This compound, with the double proportion of oxygen, is indeed known (it is hydrogen peroxide), and is the only other known compound of these two elements.

This theory fully explains why the combining proportions of

each element, in different compounds, can always be expressed by a fixed, unit number (which represents the weight of the ultimate particle of that element), multiplied, when necessary, by a whole number (representing the number of particles of the element required to form a particle of the compound in question).

This explanation was first offered by Dalton, a schoolmaster of Manchester, in 1802. Borrowing an idea from the speculations of the Greek philosophers, he called the particles of elements **atoms** (Gk. *ἄτομος*, not cut, or not divided). The atoms of any one element are all alike in weight, as well as in other properties, but the atoms of different elements differ in weight.

The particles made by uniting two or more atoms, as in forming a particle of a compound, are called **molecules** (Dim. of Lat. *moles*, a mass).

The chemical combination of two simple substances consists, then, in an elaborate re-grouping of the atoms of both elements so that molecules of the compound are formed. Definite proportions by weight are required, in order that the atoms of each element may be available in the correct proportion, 1 atom : 1 atom or 1 : 2 or 2 : 3, or in some similar, usually simple ratio.

The result was called the **atomic theory**. For long it remained an hypothesis. Recently, however, we have obtained independent proof that molecules and atoms are real, for we can now count and weigh individual molecules, and we even know something of the inside structure of atoms.

The fundamental numbers, one for each element, being the **relative weights of the atoms**, are called **atomic weights**.

**Atomic Weights Again.** — It was noted above (p. 63) that the atomic weights are often multiples of the equivalents by whole numbers. Thus, the equivalent of aluminium is 9.03, and the atomic weight 27.1; the equivalent of oxygen 8 and the atomic weight 16. This multiplication was made to obtain the true relative weights of the atoms. No facts discussed in this chapter can enable us to decide upon the relative weights of the atoms. In a later chapter, however (Chap. XII), additional facts will be encountered which enable us to reach this decision. The reader, must, therefore, for the present accept the atomic weights and use them, pending the presentation of proofs that they are correct. The step from equivalents to atomic weights is taken before the justification of it can be given, because otherwise formulæ (see next chapter), which are



based on atomic weights, could not be used in the earlier chapters and so the advantages their employment offers would be sacrificed.

Attention may be called to one fact which shows that the data presented thus far do not permit us to decide upon the best final unit weights. In the table on p. 59, we find two different compounds of oxygen and copper in which the proportions are 8 : 31.8 and 8 : 63.6. Similarly, 8 parts of oxygen combine with 100.3 and with 200.6 part of mercury; and 1.008 of hydrogen with 8 and with 16 parts of oxygen. In each case, the two compounds are equally important, and there is, therefore, no basis for deciding whether to select the number 31.8 or 63.6 for the unit weight of copper, 100.3 or 200.6 for mercury 8 or 16 for oxygen. Evidently some other kind of information (see Chap. XII) is required to enable us to make the decision.

A little thought will show that the atomic weights have all the properties which we have shown to belong to the equivalent weights. The atomic weight is the unit of weight (p. 65) actually used in expressing the proportions of each element in all its compounds. The integral factors are, of course, different from those which would be employed in expressing the composition of the same substance in terms of equivalents, because many of the latter have been multiplied by small integers already in course of being made into atomic weights. But the multiplication has in every case been by an integer, so that the new numbers are just as serviceable as are the old ones (p. 62).

To the reasons given above for the choice of oxygen as the fundamental element, and the value 8 for its equivalent weight, one other may now be added. The majority of the atomic weights, calculated on this basis from the experimental results, fall so close to being integers that the nearest round numbers are exact enough for ordinary use. Thus in the above list nine of the twelve atomic weights are within 0.1 of the nearest whole number. This convenience disappears when, for example, hydrogen with the value 1 (instead of 1.008) is made the basis.

As we have seen, the chemist does not use a single unit of weight (the gram), as does the physicist. He employs a different unit of weight (the atomic weight) for each of the eighty elements. This does not represent an arbitrary decision of the chemist, however. It is due to the fact that the atoms of any one element have the same weight, but that the atoms of different elements have different weights. The atom of uranium is 238 times as heavy as that of hydrogen, and its combining proportions, therefore, are in general

greater in the same ratio, while the atoms of the other elements have weights falling between these limits.

A complete list of atomic weights is printed on the inside of the cover at the back of this book.

**Summary.** — In this chapter we have encountered three additional facts which are characteristics of chemistry. This chapter adds an important item to our statement of the scope of the science (cf. p. 54), which, therefore, now reads as follows: Chemistry deals with the *quantitative* study of the changes in composition and constitution which substances undergo and with the transformations of energy which accompany them. To express the quantitative relations which are observed, a different unit of weight is employed for each element, and is known as the atomic weight of the element.

There are other important characteristics of chemical phenomena, mostly concerned with the conditions (p. 40), but the six which have been given are sufficient, for the present, to guide us in the systematic study of the behavior of the elements and their chief compounds.

It may not be out of place to indicate which are the most important conditions.

The first condition whose influence we are likely to notice in chemical work is that of *temperature*. The accelerating effect of rise in temperature on the speed of all chemical changes (see Chap. V), and van't Hoff's law (*q.v.*) in regard to the effect of temperature on the direction of chemical change, describe the most important characteristics of this influence.

The second condition whose effects we continually observe is that of *concentration*. This, and not chemical affinity, as many suppose, determines chemical behavior in the majority of familiar actions. It is described by the law of concentration (*q.v.*), or "mass action," as it is often inappropriately called to the great detriment of clearness. Brin's method of obtaining oxygen furnishes the first conspicuous case of the influence of this condition which we shall encounter. If this and many other examples are passed over without discussion, it is only because we must wait until much chemical experience has been gained before this principle can be understood. *Pressure* is the familiar measure of concentration in gases.

A third condition of great importance in many — perhaps most — chemical actions is the presence of a *catalytic* or *contact agent* (*q.v.*).

**Exercises.** — 1. For the purpose of recording the results of quantitative experiments, why do we prefer percentages (p. 56) to the actual weights themselves?

2. To test the correctness of the statements on p. 61, take mercury

as the basal element and 250 as its combining weight, and work out from the data on pp. 59 and 60 the corresponding combining weights of the other five elements. Then show that the values obtained have the same property as have the equivalents.

3. Express in terms of atomic weights, or their integral multiples, the composition of cupric oxide, cupric chloride, sulphur monochloride.

4. Show that doubling the atomic weight of chlorine would give an available combining number.

## CHAPTER IV

### SYMBOLS, FORMULÆ, EQUATIONS, CALCULATIONS

A CONSIDERATION of the contents of the foregoing chapter will show that the complete description of a chemical change must be exceedingly involved. In a moderately complex action, such as that of sodium chloride upon silver nitrate (p. 20), we should say that sodium chloride, composed of one atomic weight each of sodium and chlorine, when brought in contact with silver nitrate, composed of one atomic weight each of silver and nitrogen and three atomic weights of oxygen, gave silver chloride, composed of one atomic weight each of silver and chlorine, and sodium nitrate, composed of one atomic weight each of sodium and nitrogen and three atomic weights of oxygen. Such a statement, while it would give all the facts in the quantitative point of view, would be difficult to grasp and lacking in perspicuity.

**Symbols and Formulæ.** — In order to represent the nature of a chemical change in a form which may be taken in at a glance, the chemist is in the habit of using certain **symbols**, first introduced by Berzelius. Thus, the letters Ag represent one atomic weight (*i.e.*, 107.88 parts) of silver (*argentum*), and O represents one atomic weight (*i.e.*, 16 parts) of oxygen. In other words, the **symbol** of an element means one chemical unit weight (atomic weight) of the element. Since the names of many elements begin with the same initial, two letters have frequently to be used to distinguish them. Thus, C stands for one atomic weight (12 parts) of carbon, Ca for one atomic weight (40.07 parts) of calcium, Cl for 35.46 parts of chlorine. When the names of the elements are not the same in all languages, resort is frequently had to Latin. Thus, Cu stands for one weight of copper (*cuprum*), Fe is used for iron (*ferrum*), Hg for mercury (*hydrargyrum*). From German we have Na for sodium (*natrium*) and K for potassium (*kalium*).

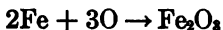
To represent a compound, the symbols of the elements which it contains are placed side by side, small numbers indicating multiples of the atomic weights where they occur. Thus, sodium chloride is represented by the symbols NaCl (= 23 of sodium to 35.46 of chlo-

rine), silver nitrate by the symbols  $\text{AgNO}_3$  (= 107.88 of silver, 14.00 of nitrogen, and  $3 \times 16$  of oxygen). Such a combination of symbols is called a **formula**. The symbols composing a formula, taken by themselves, do not stand for any definite quantity; each is one factor of a proportion. Ag means the proportion of 107.88 parts of silver to the proportions of the other elements represented by the other symbols which may be connected with it. The symbols are international (see list inside rear cover).

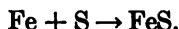
**Equations.** — It is now possible to abbreviate the condensed statements we have been using to represent the substances and their quantities in chemical reactions. Thus, the statement on p. 13, when translated into symbols, is as follows:

Iron ( $2 \times 55.84$ ) + Oxygen ( $3 \times 16$ )  $\rightarrow$  Ferric oxide (159.68)

or:



that on p. 16 is:



The chemical action above mentioned (p. 20) appears as follows:



This expression contains all that was conveyed by the words which were written out in full. The arrow indicates that the materials on the left-hand side pass, in the chemical transformation, into those on the right-hand side. Such symbolic expressions are called **equations**.

It will be observed that, in the first equation, we employ the form  $2\text{Fe}$  before combination and  $\text{Fe}_2$  (in  $\text{Fe}_2\text{O}_3$ ) after it. The reasons for this usage will become clear as we proceed. We note simply that  $2\text{Fe}$  means 2 separate atomic weights of iron, as  $3\text{Fe}_2\text{O}_3$  would mean three separate **formula-weights** of oxide of iron. The same *substance*, iron, might appear as  $5\text{Fe}$  or  $8\text{Fe}$  in other equations, according to the proportion needed. But  $\text{Fe}_2\text{O}_3$  is a group of five atomic weights united chemically. The *substance* ferric oxide never contains either more or less than two atomic weights of the *element* iron, and its formula is invariable. Thus the *regular* integers multiplying the atomic weights in the composition of a particular compound are written *after* the symbols of the elements, while more arbitrary coefficients which change from one use of the substance to another are written in front. When no coefficient appears in front of a symbol or formula, 1 is to be understood.

Much practice is required to enable one to make and understand equations. The reader should, therefore, at once turn back to the statements on pp. 13, 16, 17, 18, obtain the necessary atomic weights and symbols from the table at the end of the book, and construct the equation in each case.

We shall find later that there are two substances containing nothing but oxygen, and that each is a compound of the element with itself. The molecular formulæ of these two are  $O_2$  (oxygen) and  $O_3$  (ozone). Thus O or 2O or 3O would all be used for different proportions of the substance O, if such a substance were known, and O would be used for a substance made of oxygen, but different from oxygen or ozone. Molecular formulæ will not be employed here until after Avogadro's law has been discussed. They will then be used exclusively.

The object in writing a series of formulæ in the above manner is to show that the system upon the left-hand side, consisting of certain substances whose composition and properties we know, is, under the conditions of the experiment, unstable, and changes into the system upon the right-hand side, whose nature we also know. The materials on the two sides are essentially different, for the transformation represented is a chemical *change*. It is somewhat anomalous, therefore, that, to connect two sets of things which are essentially different, the sign = is usually employed. To call this a *chemical* equation is still more anomalous, since it is precisely in the chemical point of view that the difference between the two sides is most strongly to be emphasized. It represents two sets of things which are different, and not alike chemically. The physical properties of the two sets of substances are likewise totally unlike. There is only one respect in which the materials on the two sides agree, and that is that their mass is not different. This is, however, merely an example of the law of conservation of matter, and need not, therefore, be specially commemorated in the form in which we write every equation. It may be assumed that the equality in mass holds for all chemical changes until some case where it does not hold shall have been discovered. Above all it must be remembered that the chemical equation is not an algebraic expression; it is not subject to the rules of algebra. It is a brief expression, in terms of the atomic weights, of the distribution in kind and quantity of the constituents of a system before and after chemical change.

**Making Formulæ.** — To make the formula of a compound substance, assuming the formula to be unknown, two kinds of information are required. We ascertain (1) by *measurement* the proportion by weight of the constituents in the compound. We require also (2) to know the chemical unit weights — the atomic weights — which have been accepted by chemists for each constituent element. By factoring the terms of the first proportion so that one factor in each case is the atomic weight, we discover whether multiples of the atomic weights will be required to represent the composition of the sub-

stance, and if so what these must be. An illustration will make the process clear.

Suppose the problem is to make the formula of dried rust. By weighing before and after the change, we get the weight of the iron and of the corresponding amount of oxygen in the rust it produces. If we took 2 g. of iron we should get about 2.86 g. of rust. So that

the proportion of iron to oxygen is  $\frac{2}{0.86}$ . Now, in the formula, the

same ratio must be represented by means of multiples of the atomic weights (p. 69). We therefore divide the quantity of each element by the corresponding atomic weight. This gives us the factors by which the atomic weights are to be multiplied. The atomic weights are 55.8 and 16 respectively:  $2 \div 55.8 = 0.0358$ , and  $0.86 \div 16 =$

0.0537. The proportion  $\frac{2}{0.86}$  then becomes  $\frac{55.8 \times 0.0358}{16.0 \times 0.0537}$ . Now

this proportion must be capable of expression in terms of *integral* multiples of the atomic weights. We find that the greatest common measure of the two factors is 0.0179. Dividing above and below by

this, we obtain the ratio  $\frac{55.8 \times 2}{16.0 \times 3}$ . Substituting the symbols for the

atomic weights, the proportion appears as  $\frac{\text{Fe} \times 2}{\text{O} \times 3}$ , and the formula is therefore  $\text{Fe}_2\text{O}_3$ .

Applying the same process to cupric oxide (p. 56), we start with the result of the measurement: copper : oxygen :: 85 : 21.

$$\frac{\text{Copper}}{\text{Oxygen}} = \frac{85}{21} = \frac{63.57 \times 1.3}{16 \times 1.3} = \frac{\text{Cu} \times 1.3}{\text{O} \times 1.3} = \frac{\text{Cu}}{\text{O}} \text{ or } \text{CuO}.$$

If the composition of the substance has been stated in percentages, the same device is used. Thus, the case of sodium sulphate works out as follows:

Element.	Percentage.	At. Wt.	Quotient	+	Formula
Sodium . . . . .	32.43	23	$\times 1.41$	0.705	$\text{Na} \times 2$
Sulphur . . . . .	22.55	32	$\times 0.705$	0.705	S
Oxygen . . . . .	45.02	16	$\times 2.814$	0.705	$\text{O} \times 4$

The formula is, therefore,  $\text{Na}_2\text{SO}_4$ .

It is obvious that, after we have found out what elements compose a given compound, we are still unable to write its formula. We

may *not* simply set the symbols down, side by side. A measurement must be made, in order that we may find out the factors by which the atomic weights are to be multiplied.

**Writing Equations.** — To make the equation representing a chemical change we take the following steps:

1. We note the formulæ of the substances used.
2. We recognize by their properties the substances produced, and learn their formulæ. This we do, either by measurement and calculation, as shown above, or we find in a book the formulæ as they have been determined by the experimental work of chemists.
3. We then write a skeleton equation. In the first example discussed above (p. 70), this is:

*Skeleton equation:*  $\text{Fe} + \text{O} \rightarrow \text{Fe}_2\text{O}_3.$

We are careful to place the substances used on the left, and to point the arrow towards those which are produced.

4. Finally, we balance the equation, by placing the proper coefficients before the formulæ. This last operation requires experience for its rapid performance. A good rule is to begin by picking out that one of the formulæ which contains the largest number of atomic weights, no matter upon which side it appears. Here, this formula is  $\text{Fe}_2\text{O}_3$ . We then reason that, to obtain  $\text{Fe}_2$  we require  $2\text{Fe}$ , and to obtain  $\text{O}_3$  we require  $3\text{O}$ , and accordingly we place these coefficients before the appropriate symbols, thus:

*Balanced:*  $2\text{Fe} + 3\text{O} \rightarrow \text{Fe}_2\text{O}_3.$

It is hardly necessary to add that a chemical equation gives the proportions of the materials and nothing more. The physical conditions, for example, whether the substances are dissolved in a liquid, or are in the state of gas, or are at a high temperature, have no place in it. The physical properties of the substances concerned, and also the energy in the form of heat or electricity which may appear or disappear in the process, are likewise left entirely out. A question in regard to the nature of a particular chemical change demands in answer a full statement of all these things. The equation is therefore an essential part, but only a part, of such a statement.

That the formulæ and equations can deal only with the *material* part of the substances undergoing change, and not with their energy (p. 35), is shown by a moment's consideration. Consistency is to be secured only by holding that the



symbol S, whether alone or combined with others, stands for the matter-part of the sulphur (for the element, in fact, see p. 23). It is 32 parts by weight of sulphur-matter. Only in this way does it preserve the same significance on both sides of the equation  $S + O_2 \rightarrow SO_2$ . If S on the left side stood for the *free substance sulphur*, then it would stand for 32 parts of sulphur-matter plus the appropriate amount of energy. In this case the S on the right side would have a different signification, and represent a less amount of energy. This is only the beginning of the difficulty, for we then find that S in  $H_2SO_4$  represents the same weight of sulphur-matter with still another proportion of energy, and S has as many interpretations as there are formulæ in which it occurs. Clearly, all references to energy should be rigidly excluded from equations, and thermochemical data can never be given in connection with them without complete sacrifice of consistency. In this book, however, the habit of writing thermochemical equations, being universal, is frequently followed when thermochemical data are given.

**Units of Measurement in Chemical Work.** — In chemical work temperatures are invariably measured on the Centigrade scale. The temperature of a mixture of ice and water is the zero point. The temperature of the steam which rises from water boiling under a pressure of one atmosphere is represented by  $100^\circ$ . The interval between those two points is divided into one hundred equal parts.

For the expression of length, weight, and volume, the metric system is employed. The unit of this system is the meter, which is subdivided into decimeters, centimeters (cm.), and millimeters (mm.). For small measurements the last subdivision is taken as the unit. A cubic centimeter (c.c.) is the unit of volume for small measurements. For larger ones the liter, which contains 1000 cubic centimeters, is used. The unit of weight is that of one cubic centimeter of water at  $4^\circ$ , the temperature of maximum density. This is called the *gram*.\* For larger amounts of material the kilogram, which contains 1000 grams (1000 g.), is frequently employed. The meter is equal to about  $39\frac{1}{2}$  inches in ordinary measures, and the centimeter is very nearly  $\frac{1}{2}$  of an inch. One liter is about  $\frac{1}{16}$  of a cubic foot and contains 61 cubic inches. One hundred grams is about  $3\frac{1}{2}$  ounces avoirdupois, and one ounce equals 28.35 grams (see Appendix I).

**Calculations.** — As we have seen (p. 69), the formula represents the composition of a substance, using the atomic weights as the units. We have learned how the formula is calculated from measure-

\* In point of fact, the gram is the one-thousandth part of the weight of the standard kilogram kept in Paris. This differs from the weight of 1 c.c. of water at  $4^\circ$  by less than 0.01 per cent.

ments made in an experiment (p. 72). We may now take up some of the ways of using the information contained in a formula.

**Composition from the Formula. Formula-Weight.** — To learn the composition of a substance, such as potassium chlorate  $\text{KClO}_3$ , from its formula, we look up the values of the atomic weights (inside rear cover). We find  $\text{K} = 39.1$  parts of potassium,  $\text{Cl} = 35.46$  parts of chlorine, and  $\text{O}_3 = 3 \times 16$  or 48 parts of oxygen. The proportions, in order, are therefore: 39.1 : 35.46 : 48.

What is the proportion of oxygen to potassium and chlorine, together? It is  $48 : 39.1 + 35.46$ , or  $48 : 74.56$ , or  $1 : 1.55$ .

We require a name for the sum of the weights of the constituents indicated in the formula. This is called the **formula-weight**. Thus, for potassium chlorate, it is  $39.1 + 35.46 + 48$ , or 122.56.

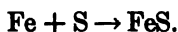
**To Find the Percentage Composition.** — In potassium chlorate the proportions are 39.1 of potassium, 35.46 of chlorine, and 48 of oxygen or a total of 122.56. In one hundred parts, the potassium is  $\frac{39.1}{122.56} \times 100$ , or 31.9; the chlorine  $\frac{35.46}{122.56} \times 100$ , or 28.9; and the oxygen  $\frac{48}{122.56} \times 100$ , or 39.1.

Stated in terms of the rule of proportion, we have, for the potassium,  $122.56 : 39.1 :: 100 : x$ , where  $x$  is the percentage of potassium.

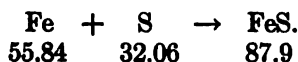
**Calculations by Use of Equations.** — We frequently wish to know what weight of a product can be obtained from a given weight of the necessary materials, or how much material is required to furnish the desired weight of a product. For example, what weight of ferrous sulphide can be made with 100 g. of iron? It is understood that the necessary sulphur is available.

To avoid the blunders which are easily made, observe strictly the following rules:

1. Write down the equation:

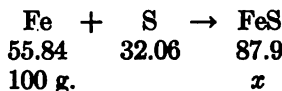


2. Place under each formula the weight it represents:



3. **Read this expanded equation:** In this case it reads: 55.84 parts of iron combine with 32.06 parts of sulphur to give 87.9 parts of ferrous sulphide.

4. **Re-read the original problem:** "What weight of ferrous sulphide can be made with 100 g. of iron?" Having done this, place the amount given in the problem (100 g. of iron) under the formula of the substance in question. Then notice what the problem asks ("what weight of ferrous sulphide") and place an  $x$  under the formula of that substance:



5. **Read the problem as now tabulated:** 55.84 g. of iron give 87.9 g. of ferrous sulphide, therefore 100 g. of iron will give  $x$  g. of ferrous sulphide.

6. **State the proportion in this order** (or, see below):

$$55.84 : 87.9 :: 100 : x \quad (= 157.5 \text{ g.}).$$

If the tabulation in rule 4 has been prepared correctly, this final statement as a proportion is purely mechanical. It will be noted that only two of the three quantities given in the expanded equation were actually used.

6a. **Alternative method:** At the sixth step, we may also say: If 55.84 g. of iron give 87.9 g. of ferrous sulphide, 1 g. of iron will give  $\frac{87.9}{55.84}$  g. (= 1.575 g.) of ferrous sulphide. Then, if 1 g. of iron gives 1.575 g. of ferrous sulphide, the 100 g. of iron will give  $100 \times 1.575$  g. (= 157.5 g.) of ferrous sulphide.

**Warnings.** — In solving the exercises at the end of the chapter, beware of three kinds of mistakes, which are commonly made.

1. Do not read the problem carelessly and make the equation backwards, that is, with the sides reversed. Focus attention first on the exact chemical change involved.

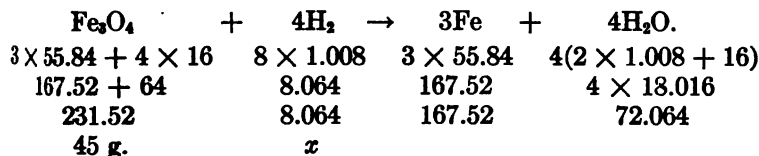
2. Do *not* speak, or think of the symbols Fe and S as standing for "1 part" of iron or sulphur. They stand for 1 *chemical unit*, or atomic weight, or atom, in each case, that is, for "55.84 parts" and "32.06 parts," respectively.

3. Follow the rules laid down above. The chemist follows these rules. The beginner always thinks he can do without them, and he fails in consequence. Writing the equation in expanded form (rule

2) and reading the problem into it (rules 4 and 5) are absolutely essential steps.

**Another Example.** — What weight of hydrogen is required to reduce 45 g. of magnetic oxide of iron to metallic iron?

Following the rules, as before, we reach the expanded equation:



Observe that the atomic weights are multiplied by the sub-numbers, so that, for example,  $\text{Fe}_3 = 3 \times 55.84$ . Observe also that the formula-weights are multiplied by the coefficients, when such occur, in front of the formulæ, so that, for example,  $4\text{H}_2\text{O} = 4 \times 18.016$ .

The proportion  $231.52 : 8.064 :: 45 : x (= 1.57)$  supplies the answer, 1.57 grams of hydrogen.

Using the alternative plan: If 231.52 g. of magnetic oxide are reduced by 8.064 g. of hydrogen, 1 g. will be reduced by  $\frac{8.064}{231.52}$  g. (= 0.035 g.) of hydrogen. Hence, if 1 g. of magnetic oxide is reduced by 0.035 g. of hydrogen, 45 g. will be reduced by  $45 \times 0.035$  g. (= 1.57 g.) of hydrogen.

**Exercises.** — 1. What weight of mercury is obtained from 120 g. of mercuric oxide?

2. What weight of mercuric oxide will furnish 20 g. of oxygen?

3. What weight of silver chloride is obtained from 50 g. of silver nitrate (p. 70)?

4. What weight of rust may be obtained from 10 g. of oxygen?

5. How much silver is contained in 100 g. of an impure specimen of silver chloride which is 33 per cent sand?

6. If 26 g. of mercurous oxide are required to give, by heating, 1 g. of oxygen, what is the formula of the substance?

7. What are the formulæ of the substances possessing the following percentage compositions (p. 72).

I	
Magnesium,	25.57
Chlorine,	74.43

II	
Sodium,	32.43
Sulphur,	22.55
Oxygen,	45.02

III	
Potassium,	26.585
Chromium,	35.390
Oxygen,	38.025

8. What are the percentage compositions of hausmannite  $\text{Mn}_3\text{O}_4$ , potassium bromide  $\text{KBr}$ , ferrous sulphate  $\text{FeSO}_4$ ?

9. What weight of hydrogen is required to reduce 100 g. of ferric chloride  $\text{FeCl}_3$  to ferrous chloride  $\text{FeCl}_2$  (hydrogen chloride  $\text{HCl}$  is formed)?

10. Which law of chemistry permits us to use symbols in expressing the compositions of substances?

11. Calculate the formula of the oxide of tin formed when 2 g. of tin give 2.54 g. of the oxide.

## CHAPTER V

### OXYGEN

WE begin the more systematic study of chemistry with oxygen, for it is a most interesting as well as useful substance. It is the active substance in the air. We depend upon it for *life*, since in its absence we suffocate, for *heat*, since wood, coal, and gas will not burn without it, and even for *light* where oil, gas, or a candle is employed.

We wish to know with which substances we use in the laboratory it can combine, as well as the substances on which it has no action. This information will show us how to work, in future, without interference from the oxygen in the air and whether oxygen has probably played a part in some experiment or not.

We take up, then, (1) the **history** of the element, (2) what materials contain oxygen (**occurrence**), (3) how we can obtain it in a pure state (**preparation**), (4) what its **specific physical properties** as a substance are, and (5) what it does, and what it can not do in nature and in the laboratory (**chemical properties**). The classification of the facts about this, and other substances, under five heads is somewhat mechanical, but has the advantage of enabling the reader quickly to find any required information.

**History of Oxygen.**— While many elements which are less easily obtainable than oxygen have been recognized as distinct substances for many centuries, oxygen did not attain this position until the end of the eighteenth century. The reason of this was that gases are not so easy to handle and distinguish as are solids or liquids, and consequently very slow progress was made in the study of them.

The Chinese, in or before the eighth century, knew that there were two components in the air, and that the active one, *yin*, combined with some metals, and with burning sulphur, and charcoal. They even knew that it could be obtained in pure form by heating certain minerals, of which one was saltpeter. Leonardo da Vinci (1451-1519) was the first European to state that the air contained two gases. Mayow (1669) measured the proportion of oxygen in the air and discussed fully its uses in combustion, rusting, vinegar-

making, and respiration, but did not make a pure sample. Hales (1731) made it by heating saltpeter, and measured the amount obtainable, but did not see any connection between it and the air! Bayen (April, 1774) was the first to make it by heating mercuric oxide. Priestley\* was particularly interested in examining the nature of the gases which were evolved by some materials when heated. His plan was to fill an elongated glass vessel with mercury (Fig. 25); to invert this in a trough filled with the same metal, and, after allowing the substance under examination to float up into the top of the tube above the mercury, to expose it to the rays of the sun concentrated by a large burning lens. Priestley found (Aug. 1, 1774) that one material, then known as "*mercurius calcinatus per se*"

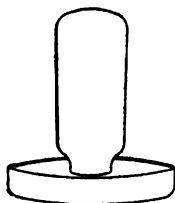


FIG. 25.

(mercuric oxide), gave off an unusual amount of a gas, or "air" as he called it. Quite purposelessly, as he admits, he thrust a lighted candle into it and was delighted with the extreme brilliance of the flame. He had, however, no notion until a year later that it was a component of the air. Even then, he thought it was a compound of nitric acid, earth, and phlogiston! Scheele, a Swedish apothecary, had made it in 1771-2 from no less than seven different substances and understood clearly that atmospheric oxygen combined with metals, phosphorus, hydrogen, linseed oil, and many other substances. But his book was not published until 1777, and Priestley is usually credited with the "discovery" of the element!

Lavoisier at first (1773-5) thought that air was composed of nitrogen and "fixed air" (carbon dioxide). Although Priestley had dined with him (Oct., 1776), and communicated his discovery, so far as he understood it himself, yet when Lavoisier heated mercuric oxide in March, 1775, he expected to obtain "fixed air." Later in the same year, Lavoisier held that air contained no "fixed air," and was made up of a single gas. It was not until 1777 that he heated the metal mercury in a retort (Fig. 26), the neck of which projected into a bell-jar standing in a larger dish of mercury. The air, thus enclosed within the jar and the retort, during twelve days lost one-

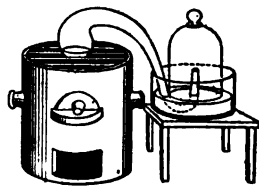


FIG. 26.

\* An English nonconformist minister who occupied his leisure time with experiments in chemistry. He afterwards moved to the United States, and died in Northumberland, Pa.

fifth of its volume. Simultaneously, red particles of mercuric oxide accumulated on the surface of the mercury in the retort. The residual gas no longer supported life or combustion, and hence was named by Lavoisier "azote" (Gk.  $\alpha$ , priv. and  $\zeta\omega\eta$ , life). In English it is called nitrogen. The oxide, on being heated more strongly by itself, gave off a gas, the volume of which exactly corresponded with the shrinkage undergone by the enclosed air, and this gas possessed in an exaggerated degree the properties which the air had lost. The proof that oxygen was a component of the atmosphere was therefore complete. Lavoisier, in the mistaken belief that the new element was an essential constituent of all sour substances, named it **oxygen**, or acid-producer (Gk.  $\acute{\alpha}\xi\acute{\iota}\varsigma$ , an acid,  $\gamma\epsilon\nu\acute{\alpha}\nu$ , to produce). Cavendish pointed out almost immediately that there were sour-tasting substances which contained no oxygen, so that the name has no longer any significance. It may here be noted that hydrogen is the only element which is found in all acids.

**Occurrence.** — As we have seen (p. 24), nearly 50 per cent of terrestrial matter is oxygen. Water contains about 89 per cent, the human body over 60 per cent, and common materials like sandstone, limestone, brick, and mortar more than 50 per cent of this element in combination. One-fifth by volume (nearly one-fourth by weight) of the air is *free* oxygen.

**Preparation of Oxygen.** — 1. The oxygen of commerce is now made chiefly from **liquefied air** (*q.v.*). The liquid oxygen boils at  $-182.4^{\circ}$ , but the nitrogen boils at an even lower temperature ( $-194^{\circ}$ ). As the liquid air has a temperature of about  $-190^{\circ}$ , somewhat above that of boiling nitrogen, the latter evaporates much more freely than the oxygen. After a time, when the remaining liquid is almost pure oxygen (96%), the gas coming off is compressed by pumps (100–150 atmos.) into the steel cylinders (Fig. 27) in which it is sold. In medicine, patients suffering from pneumonia or suffocation obtain some relief by inhaling it in this form. It is also used in feeding flames, instead of air, when intense heat is required (see acetylene torch and calcium light).

2. Unfortunately, it is difficult to liberate oxygen from **natural substances**. Saltpeter (potassium nitrate  $\text{KNO}_3$ ), for example, which is found in many soils, and can be

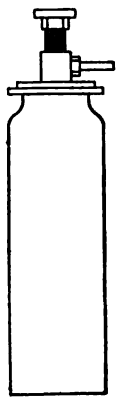


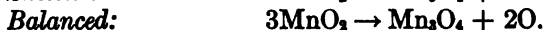
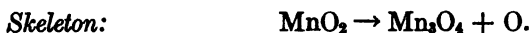
FIG. 27.



dissolved out with water, gives off oxygen (p. 79) only when raised to a bright red heat by the Bunsen flame or blast lamp. But, even at this temperature, it gives up only one-third of the oxygen it contains, leaving potassium nitrite  $\text{KNO}_2$ :

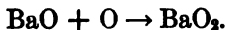


The mineral pyrolusite (manganese dioxide  $\text{MnO}_2$ ), employed by Scheele, requires a higher temperature. It usually contains the elements of water, also, and gives off water vapor at the same time. An oxide of the composition  $\text{Mn}_3\text{O}_4$  remains:



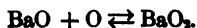
3. In practice, we are compelled to use manufactured substances. Amongst these are mercuric oxide, expensive, but historically interesting (p. 80); barium peroxide, formerly used in manufacturing oxygen on a large scale (Brin's process); potassium chlorate (see below), the most convenient for laboratory use; and sodium peroxide. Many other substances of this class will be encountered in the sequel.

**Brin's Oxygen Process.** — This starts from barium oxide (*q.v.*). Barium oxide  $\text{BaO}$  closely resembles quicklime  $\text{CaO}$ , but differs from this substance in the fact that, when heated in air to about  $500^\circ$ , it rapidly acquires additional oxygen and gives barium peroxide  $\text{BaO}_2$ . When barium peroxide is raised to  $1000^\circ$ , this extra oxygen is given up again. Barium oxide contains one chemical unit weight each of the two constituents and takes up another unit of oxygen, so that the equation for the primary action is:



The subsequent decomposition of the peroxide, during the stage in which the oxygen is made, is the exact opposite:  $\text{BaO}_2 \rightarrow \text{BaO} + \text{O}^*$ . The commercial advantage of the method lies in the fact that the barium oxide, remaining after the second stage, can be used over and over again. This, as will be seen, is in reality a chemical method of obtaining oxygen from the air.

\* In cases where an action is reversible, and the direction depends on conditions which may be altered, we write both equations in one:



In practice an improvement on the above principle makes working more economical. It is found that if the barium oxide is maintained at a temperature of  $700^{\circ}$ , intermediate between the two just mentioned, oxygen is absorbed when air is forced under pressure into the tubes containing the oxide. A valve at the extremity of the tubes permits the escape of the nitrogen. When the combination with oxygen is completed, the pumping apparatus is reversed and, a partial vacuum being created, the oxygen in combination is given off without any alteration in temperature being necessary. Thus a great waste of fuel is avoided, and the process is rendered more nearly continuous.

**Oxygen from Potassium Chlorate.**— This is a white crystalline substance used in large quantities in the manufacture of matches and fireworks. When heated in a tube similar to that in Fig. 9, it first melts ( $351^{\circ}$ ) and then, on being more strongly heated, it effervesces and gives off a very large volume of oxygen. Examination shows that the whole of the oxygen it contains can be driven out. The white material which remains after the heating is potassium chloride and, when decomposed, it yields potassium and chlorine in the exact ratio of their atomic weights. Its formula is thus  $KCl$ . We may infer, therefore, that the composition of the original substance will be representable by the formula  $KClO_x$ , where  $x$  is the number of atomic weights of oxygen. Measurement and calculation show  $x = 3$ . The formula is therefore  $KClO_3$ , and the equation for the decomposition (see, however, under Perchlorates):



To learn the value of  $x$ , we ascertain the loss in weight (= oxygen) which a known quantity of potassium chlorate sustains when heated in a hard glass tube closed at one end. By subtraction we get the weight of potassium chloride formerly combined with the oxygen. In an actual experiment, 2.998 g. of potassium chlorate gave 1.169 g. of oxygen and left 1.829 g. of the chloride. The atomic weights of potassium and chlorine are 39.1 and 35.46 respectively, and the formula-weight of the chloride is therefore 74.56. Dividing the measured weights of oxygen and potassium chloride by the corresponding atomic and formula-weights (cf. p. 72), respectively:  $1.169 \div 16 = 0.07306$  and  $1.829 \div 74.56 = 0.02452$ . We observe that the ratio of the quotients is  $2.98 : 1$ , or almost exactly  $3 : 1$ . The formula is therefore  $O \times 3, (KCl) \times 1$ , or  $KClO_3$ .

A peculiarity of this action is that admixture of manganese dioxide increases very markedly the speed with which the decomposition of the potassium chlorate takes place. Hence, in its presence, and it is

generally mixed with the chlorate in laboratory experiments (Fig. 28), a sufficient stream of the gas is obtained at a relatively low temperature (below  $200^{\circ}$ , see p. 97). Hales (p. 80) was the first to collect a gas over water, in order that it might be kept unmixed with air.

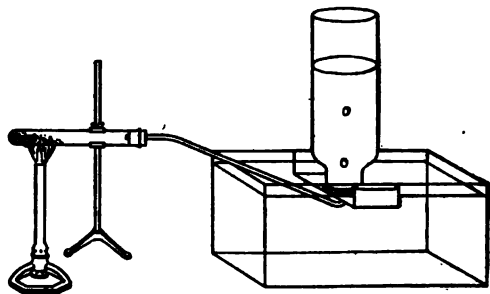


FIG. 28.

***Familiarity with Physics Required in the Study of Chemistry.*** — In mentioning chemical phenomena, it is inevitable that considerations of space should limit our statements to the merest indication of the process and the briefest record of the chemical result. The prodigious disproportion between the meagerness of this fragment and the mass of detail which lies behind it in each case should be constantly before the mind of the reader. The book gives empirical knowledge, the laboratory work and the discussion of it furnish the only real knowledge. The extent and nature of this real knowledge may be shown in connection with any action. As an illustration we may point out some of the problems which the heating of potassium chlorate presents to one who is trying to acquire an intelligent acquaintanceship with its chemistry, and has not previously done the experiment.

First, the substance melts. It must be realized that this is a common occurrence which does not necessarily imply any profound change, and may be reversed by cooling. Later, the liquid appears to boil, and the properties of a boiling substance must be known. If the observer has been informed in advance that the body is homogeneous, he must know that, if it is simply boiling, it will evaporate completely and leave nothing behind, and that the temperature required to achieve this will remain constant from the beginning to the end. In order, therefore, to become aware of the fact that here decomposition is taking place, he must note the ways in which the decomposition of potassium chlorate differs from ordinary boiling. For example, if it were a case of boiling, he should expect to find the solid body condensing on the sides of the tubes, and note the fact that no such condensation is observed, with the appropriate inferences. He should observe that, in the later stages at least, the escape of the gas does not cease when the flame is removed, although this would undoubtedly occur in a case of simple boiling. He must further observe the changes in the consistency of the material and the way in which it finally becomes thick and may even solidify. Even the most ex-

perienced investigator would have to make many careful experiments before he could definitely classify the nature of the phenomenon being observed. The first inference would probably be that the phenomenon was certainly not one of mere ebullition. In some ways it is like the evaporation of a solution, obtained, say, by the melting of a substance in its own water of crystallization. Yet, this hypothesis would not explain to the thoughtful observer even the more obvious features of the phenomenon, for the liquid which was acting as a solvent would have to be amazingly volatile if the absence of any condensation on the walls of the tube was to be accounted for.

The illustration need not be elaborated further. These remarks are sufficient to show that even the simplest experiment presents an almost limitless field for the discussion of important questions which are more or less common to all chemical phenomena. It must be noted, also, that chemical change is in itself not perceptible by the senses, and that only physical properties and physical phenomena are observed (*cf.* pp. 47-49). The chemical facts, such as the general nature of the change, the conditions under which, and the facility with which it occurs, are reached solely by inference. The above example shows the ready and thorough knowledge of physics which must be at the command of every individual effort to study even the simplest chemical phenomenon. It is only when the physics as well as the chemistry of the change have been mastered that the "real knowledge" to which reference was made above has been gained.

**Oxygen from Sodium Peroxide.**—Oxygen can be obtained conveniently from sodium peroxide  $\text{Na}_2\text{O}_2$  and water  $\text{H}_2\text{O}$  by means of generators (Fig. 29) similar to the acetylene generators used on automobiles. When the metal sodium is burned in air, sodium peroxide is obtained as a powder. This powder, after being melted, solidifies in compact, solid form, and is sold as "oxone." The oxone is bought in a small, sealed tin can, the ends of which are perforated in several places just before use. When the valve (*B*) is opened, so that the oxygen escapes, the water, which fills the generator almost to the top, enters the can (*C*) by the holes in the bottom and interacts with the oxone. When the valve is shut, the gas continues to be generated until it has driven the water down again below the level of the bottom of the can:

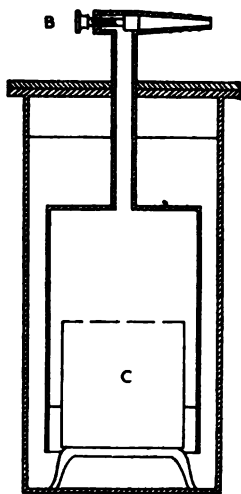


FIG. 29.

*Skeleton:*  $\text{Na}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{O}.$

*Balanced:*  $\text{Na}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{O}.$

This method is convenient because it works at room temperature and can be started and stopped at will. The sodium hydroxide produced is very soluble in water and remains dissolved. Note that the name sodium hydroxide indicates the elements which compose it.

***Specific Properties of Two Kinds, Physical and Chemical.***

— We have learned that every substance has its own set of specific properties. In describing a substance, it is convenient to divide the properties into two classes. The list of substances with which the given substance can enter into chemical combination, for example, we place under **specific chemical properties**. Relations of the substance to any of the varieties of chemical change (p. 21) belong to this class.

On the other hand, we do not consider melting or boiling to be chemical changes, so we place the temperatures at which the substance melts (m.-p.) and boils (b.-p.), its color, etc. (for list, see p. 40) under **specific physical properties**.

Properties of either class may be used for recognizing a substance.

***Specific Physical Properties of Oxygen.*** — Oxygen resembles air in having neither *color*, *taste*, nor *odor*. The *density* of a substance is, strictly speaking, the weight of 1 cubic centimeter (1 c.c.). In the case of a gas, we frequently prefer to give the weight of 1000 c.c. (1 liter), at 0° and 760 mm. (1 atmosphere) barometric pressure. For oxygen this weight is 1.42900 grams (Morley). The corresponding weight for air is 1.293, so that oxygen is slightly heavier, bulk for bulk, than air (in the ratio 1.105 : 1). Oxygen can be *liquefied* by compression, provided its temperature is first reduced below -118°, which is its critical temperature (*q.v.*). The gas is slightly *soluble* in *water*, the solubility at 0° being 4 volumes of gas in 100 volumes of water (at 20°, 3 : 100).

The solubility of oxygen in water, although slight, is in some respects its most important physical property. Fish obtain oxygen for their blood from that *dissolved* in the water. With air-breathing animals (like man), the oxygen could not be taken into the system, if it did not first dissolve in the moisture contained in the walls of the air sacs of the lungs, and then pass inwards in a dissolved state to the blood.

Liquid oxygen, first prepared by Wroblevski, has a pale-blue color. At one atmosphere pressure, that is, in an open vessel, it boils at -182.5°. Its density (weight of 1 c.c.) is 1.13, so that it is slightly denser than water. By cooling with a jet of liquid hydro-

gen, Dewar froze the liquid to a snow-like pale-blue solid. A tube of liquid oxygen is noticeably attracted by a magnet.

**Six Specific Physical Properties of Each Gas.** — Although every substance has many physical properties, we shall mention only those which are used in chemical work, with occasionally the addition of any peculiar or unexpected quality. It will aid the memory to recall the physical properties of a *gas*, if we note that, as a rule, **only six physical properties** are mentioned: (1) color, (2) taste, (3) odor, (4) density, (5) ease of liquefaction, defined by the critical temperature, (6) solubility, usually in water only.

It should be noted that, of these, the first three are never stated quantitatively. Taste and odor cannot, at present, be defined on any absolute scale. Color could be defined in terms of the wave-lengths of the light reflected and transmitted, and of the relative intensities of each wave-length, but chemists seldom attempt anything so elaborate. On the other hand, the last three are comparatively easy to measure, and are always stated quantitatively. Yet, in the case of most substances, even familiar ones, careful determinations have never been made. Thus, for potassium chlorate, the published melting-points vary from 324° to 351°!

**Solubilities of Gases in Non-Aqueous Liquids.** — Iron and steel are oiled to prevent rusting. The oil, however, does not prevent access of oxygen to the metal, for, contrary to the common impression, gases are roughly ten times more soluble in liquids like petroleum and alcohol than they are in water. Water hastens rusting, and the oil excludes atmospheric moisture, since water is insoluble in oils.

The following solubilities, expressed as the volume of the gas (at 760 mm.) dissolved by one volume of the liquid, illustrate this point.

Gas.	Petroleum.		Water.		Alcohol, 0°
	10°	20°	20°	0°	
Oxygen . . . . .	0.229	0.202	0.028	0.041	0.284
Nitrogen . . . . .	0.135	0.117	0.014	0.020	0.126
Carbon dioxide . .	1.31	1.17	0.901	1.797	4.329

**Specific Chemical Properties of Oxygen.** — The chemical properties of pure oxygen are like those of atmospheric oxygen, only more pronounced.

*Non-metallic Elements.* — Sulphur, when raised in advance to the temperature necessary to start the action, unites vigorously with oxygen (Fig. 30), giving out much heat and producing a familiar gas having a pungent odor, sulphur dioxide  $\text{SO}_2$ . This odor is frequently spoken of as the "smell of sulphur," but in reality sulphur itself has no odor, and neither has oxygen. The odor is a property of the compound of the two. The mode of experimentation can be changed and the oxygen led into sulphur vapor through a tube. The oxygen then appears to burn with a bright flame, giving the same product as before.

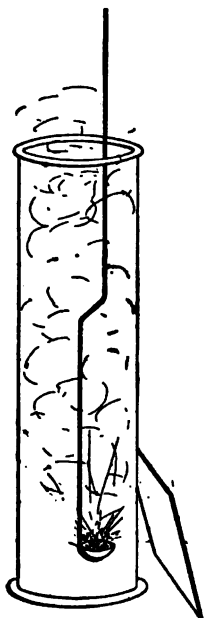
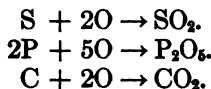


FIG. 30.

Phosphorus, when set on fire, blazes in oxygen very vigorously forming a white, powdery, solid oxide, phosphorus pentoxide  $\text{P}_2\text{O}_5$ . Burning carbon, in the form of charcoal or hard coal, glows brilliantly and is soon burnt up. It leaves an invisible, odorless gas, carbon dioxide  $\text{CO}_2$ . At high temperatures, oxygen combines readily with one or two other non-metals (*e.g.*, silicon, boron, and arsenic), and to a small extent (1% at  $1900^\circ$ ) with nitrogen. It will not combine directly with chlorine, bromine, or iodine, although oxides of the first and last can be prepared by using other varieties of chemical change. With the six members of the helium family (*q.v.*), of which no compounds are known, and with fluorine, oxygen forms no compounds.



*Metallic Elements.* — Iron, as we have seen, rusts exceedingly slowly in air (diluted oxygen) and, even when red-hot, gives hammer-scale, the black solid which is broken off on the anvil, rather deliberately. In pure oxygen, a bundle of picture-wire, if once ignited, will burn with surprising brilliancy, throwing off sparkling globules of the oxide, melted by the heat. This oxide is a black, brittle substance, identical with hammer-scale, and different from rust (ferric oxide  $\text{Fe}_2\text{O}_3$ ). It contains, in fact, a smaller proportion of oxygen

than the latter, and is called magnetic oxide of iron  $\text{Fe}_3\text{O}_4$ , identical with a well-known ore of iron.

*Skeleton:*  $\text{Fe} + \text{O} \rightarrow \text{Fe}_3\text{O}_4$ .

*Balanced:*  $3\text{Fe} + 4\text{O} \rightarrow \text{Fe}_3\text{O}_4$ .

All the familiar metals, excepting gold, silver, and platinum, when heated, combine with oxygen. Some combine more vigorously, others less vigorously, than does iron. Oxides of the three metals just named can be made by varieties of chemical change other than direct combination.

*Compound Substances*, if they are composed largely or entirely of elements which combine with oxygen, are able themselves to interact with oxygen. Usually, they produce a mixture of the same oxides which each element, separately, would give. Hence, wood, which is composed of carbon and hydrogen with some oxygen, when burnt in oxygen, produces carbon dioxide and water (oxide of hydrogen) in the form of vapor. Again, carbon disulphide burns readily, giving carbon dioxide and sulphur dioxide, just as do carbon and sulphur, separately. Ferrous sulphide gives, similarly, sulphur dioxide and magnetic oxide of iron.

**Tests: A Test for Oxygen.** — A test is a property which, because it is easily recognized (a strong color, for example), or for some other sufficient reason, is commonly employed in recognising a substance.

Oxygen, as we have seen (p. 17), when pure, is recognized by the fact that a splinter of wood, glowing at one end, bursts into flame when introduced into the gas. Only one other gas (see nitrous oxide) behaves similarly.

**Determining Formulae Again.** — To learn the exact nature of interactions like those used as illustrations above, quantitative experiments must of course be made. Thus, for example, a known weight of sulphur is placed in a porcelain boat (Fig. 31), which has already been weighed. The U-shaped tube to the right contains a solution of potassium hydroxide which is capable of absorbing the resulting gas. The oxygen enters from the left. When the sulphur is heated, it burns in the oxygen, and the loss in weight which the boat undergoes shows the amount of sulphur consumed. The gain in weight of the

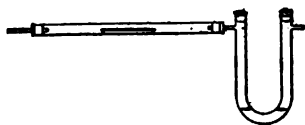


FIG. 31.



**U-tube** shows the weight of the compound produced. By subtracting, we get the quantity of oxygen. The proportion of the constituents and the steps in the calculation (p. 72) are as follows:

	PERCENTAGE		AT. WT.		FACTOR		+ 1.561
Sulphur,	50.05	=	32.06	×	1.561	= S × 1.561	S × 1
Oxygen,	49.95	=	16.00	×	3.122	= O × 3.122	O × 2

The formula of the product is therefore  $\text{SO}_2$  and the equation (p. 73) is  $\text{S} + 2\text{O} \rightarrow \text{SO}_2$ .

Similarly, phosphoric anhydride may be shown to have the formula  $\text{P}_2\text{O}_5$ , carbon dioxide  $\text{CO}_2$ , and magnetic oxide of iron  $\text{Fe}_3\text{O}_4$ .

The results given by the experiment described above (Fig. 31) are usually inexact. The tendency to the formation of sulphur trioxide, often heightened by catalytic action (see below) of the porcelain of the boat, raises abnormally the proportion of oxygen. The principle of the experiment is easy to understand, however.

In the case of phosphorus a similar plan may be used. Instead of attempting to receive the solid product in a **U-tube**, however, it must be caught by a plug of glass wool in the main tube of hard glass, and a drying tube will be needed at the end to prevent admission of moisture from the air. The increase in weight of the hard glass tube represents the oxygen taken up. Care and leisurely performance are needed to make the experiment successful.

The same method used with sulphur can be employed for carbon, since the carbon dioxide is absorbed by the potassium hydroxide. With carbon, exact results are obtained.

The data and working in these cases and in that of iron are as follows:

	PERCENTAGE		AT. WT.		FACTOR		+ 0.704
Phosphorus,	43.66	=	31.0	×	1.408	P × 2	
Oxygen,	56.34	=	16.0	×	3.521	O × 5	
							+ 2.272
Carbon,	27.27	=	12.0	×	2.272	C × 1	
Oxygen,	72.72	=	16.0	×	4.545	O × 2	
							+ 0.431
Iron,	72.38	=	55.9	×	1.295	Fe × 3	
Oxygen,	27.62	=	16.0	×	1.726	O × 4	

**Oxides: Nomenclature.**—Substances containing one element in combination with oxygen are called oxides. When the same element forms more than one oxide, the names of the oxides indicate the differing proportions. Thus we have barium oxide (or monoxide)  $\text{BaO}$ , and barium peroxide (or dioxide)  $\text{BaO}_2$ , magnetic oxide of

iron  $\text{Fe}_3\text{O}_4$ , ferrous oxide  $\text{FeO}$ , and ferric oxide  $\text{Fe}_2\text{O}_3$ . In cases like the last two the terminations *-ous* and *-ic* applied to the *metal* correspond to the smaller and larger proportions of *oxygen*, respectively, which *the metal is able to hold in combination*. The same terminations are used to distinguish chlorides, sulphides (p. 59), and other compounds, when more than one of each is known.

The discussion of the formation and properties of ozone (*q.v.*), which is an oxide of oxygen, cannot be taken up until we are in possession of the means of understanding the difference in density of the two substances (Chap. XII).

**Combustion.** — Since oxygen is a component of the atmosphere, chemical actions in which it plays a part are familiar in daily life. Violent union with oxygen is called in popular language **combustion** or burning. Yet since oxygen is only one of many gaseous substances known to the chemist, and similar vigorous interactions with these *gases* are common, the term has no scientific significance. The union of iron and sulphur, for example, gives out light and heat, and is quite similar in the chemical point of view to combustion.

**Oxidation.** — A number of cases of the union of an elementary substance with oxygen have been referred to (pp. 88, 89). In each case the substance was heated strongly and the union with oxygen was rapid (combustion). Cold oxygen, either pure or as it is found diluted in the air, however, acts upon cold substances in like manner. One difference is that in the cold the action is much slower, and oxidation (rusting) of the whole specimen may occupy months or even years. Another difference is that the products of slow and of rapid oxidation are not always identical in composition and properties. In the case of iron, for example, burning gives us the magnetic oxide  $\text{Fe}_3\text{O}_4$ , while rusting in moist air yields a hydrated ferric oxide  $\text{Fe}_2\text{O}_3 + \text{Aq.}^*$  The products differ in composition, but are nevertheless closely related.

This process of slow oxidation, although less conspicuous than combustion, is really of greater interest. Thus the **decay** of wood is simply a process of oxidation whereby the same ultimate products (namely, carbon dioxide and water) are formed as by the more rapid, ordinary combustion. Again, large volumes of pure water

\* The formula  $\text{H}_2\text{O}$  may not be used excepting to indicate a definite proportion of the elements of water (18 parts). Where the proportion varies according to circumstances, as here and in the case of solutions, the contraction *Aq.* is employed.

are mixed with **sewage**, the object being, not simply to dilute the latter, but to introduce water containing oxygen in solution. This has an oxidizing power like that of oxygen gas and, through the agency of bacteria, quickly renders dissolved organic matters innocuous by converting them for the most part into carbon dioxide and water. Thus a few miles further down the stream, the water becomes as suitable for drinking as it was before the sewage entered.

**In our own bodies** we have likewise a familiar illustration of slow oxidation. Avoiding details, it is sufficient to say that the oxygen, from the air taken into the lungs, combines with the hæmoglobin in the red blood-corpuscles. When blood is placed under the air pump, it effervesces, and oxygen is given off (Mayow, 1669). In this form of loose combination, it is carried by the blood throughout our tissues and there oxidizes the foodstuffs which have been absorbed during digestion. The material products are carbon dioxide and water, of which the former is carried back to the lungs by the blood-serum, and finally reaches the air during exhalation. The important product, however, is the heat, given out by the oxidation, which keeps the body warm. If we cease to eat, we become lighter and weaker, showing that a real portion of our structure is gradually being consumed by oxidation.

The opposite of oxidation, the *removal* of oxygen, is spoken of in chemistry as **reduction**. But this term, as we shall see, like oxidation, has been stretched to cover other kinds of chemical change.

**Uses of Oxygen.**—A number of the practical applications of oxygen have already been mentioned. For example, in the foregoing section we have referred to its use in breathing, its rôle in decay, which is a beneficent process because it removes much useless matter which might otherwise cause disease, and its value in the disposal of sewage. Power and heat for commercial purposes are almost all obtained by the burning of coal, in which oxygen from the air plays a large part. If we had to purchase the oxygen as well as the coal, we should require at least three tons of oxygen for every ton of coal.

Oxygen in cylinders, and from oxygen generators, is used to restore the supply in the atmosphere of submarine boats, as well as for the purposes already mentioned (p. 81).

**Substances Indifferent to Oxygen.**—Finally, since the atmosphere contains so large a proportion of oxygen, substances which

do *not* oxidize and, when heated, do *not* burn, have many uses. Gold, silver, and platinum are of this kind and are used for ornaments. The last is used for crucibles in which bodies are heated in the laboratory. Although iron burns in pure oxygen, it does not oxidize rapidly in the air even when heated, and so is used for making vessels for cooking and in constructing fire-proof buildings.

Compounds, already fully oxidized, are naturally not combustible. Of this nature are sandstone, granite, brick, porcelain, glass, and water. All these are, therefore, fireproof. Moreover, these substances do not give off oxygen when heated (steam decomposes slightly). Glass and porcelain thus neither lose nor gain in weight when heated, and are suitable materials for laboratory apparatus.

**Activity and Stability.** — A substance which enters in combination vigorously, as does oxygen, is called chemically active. Nitrogen, on the other hand, is relatively inactive. An active element, since it combines eagerly, naturally holds tenaciously to the matter with which it has combined. An active element implies, therefore, also one which is in general difficult to liberate from combination. Its compounds are in general relatively **stable**. Thus, many oxides, and the natural compounds just mentioned (sandstone, granite, brick, and porcelain, the last two made from clay), do not lose oxygen even at a white heat and are very stable.

***Means of Altering the Speed of a Given Chemical Action:***

***By Change of Temperature.*** — That the same change may proceed with very different speeds according to conditions is a familiar fact. For example, **raising the temperature increases the rapidity of all chemical interactions**. Thus, cold iron combines with oxygen very slowly, giving rust, while white-hot iron sheds quantities of scales of an oxide, formed in the few moments that it is under the blacksmith's hammer. White-hot coal unites with oxygen in the air to form carbon dioxide and seems to disappear before our eyes, while in the cellar, even in warm weather, we observe no appreciable diminution in its amount. Careful measurement, however, shows that, when stored in the open air, coal does lose from 2 to 10 per cent of its combustible matter. When air is largely excluded, say, by storage under water, there is no loss. No temperature can be found at which the interaction definitely begins. We believe that every such change proceeds with *some* speed at every temperature. A rough estimation, based on experiment, shows that on an average,

other things being equal, every rise in temperature of ten degrees doubles the amount of material changed per second, and conversely.

If, on bringing two materials together, the chemist observes marks of chemical action, he immediately begins cautiously to heat the mixture. This appeal to the magnifying effect of a rise in temperature is always made as a matter of course.

The common expressions used in chemistry in describing temperatures, along with the corresponding readings of the thermometers are as follows:

Incipient red heat, about 525°.	Yellow heat, about 1100
Dark red heat, " 700°.	Beginning white heat, " 1300
Bright red heat, " 950°.	White heat, " 1500

**Rapid Self-sustaining Chemical Action and Means of Initiating it.** — When a piece of wood is set on fire at one end, the heat produced by the action itself raises the temperature of neighboring portions until their speed of union becomes equal to that of the part originally lighted. In this way the whole becomes finally inflamed. When we blow the blaze out, the great excess of cold air suddenly lowers the temperature of the wood, and of the gas rising from it, and rapid union ceases. Cold water, naturally, lowers the temperature even more promptly. Whether a given set of materials can maintain itself at a temperature proper to violent interaction will depend on the amount of heat developed by the action itself on the one hand, and the losses of heat by conduction and radiation on the other. If the latter are great, the former must be greater. Thus the union of iron and oxygen *per se* gives heat enough to warm the materials to the burning temperature and leaves much over for radiation. But iron in air, which is four-fifths nitrogen, can receive the oxygen only one-fifth as fast at the start, and even more slowly as, later, the nitrogen accumulates round it. And besides, all the nitrogen has to be heated to, perhaps, 2000°. The task is too great. The union is impeded and the iron is not oxidized fast enough to generate the heat required to maintain everything at this high temperature. Poor conductors of heat, like wood and candles, far better. Powdered iron, with its particles presenting large surface to the air relatively to the weight of material in each particle to be heated, burns well.

The initial supply of heat required to start violent exothermic chemical actions, of which alone we are here speaking, must not be

confused with the heat subsequently developed as the action proceeds. The latter is usually much greater. Indeed, the *preliminary supply* varies with circumstances, and may be made as small as we choose by limiting the area first heated and using ordinary precautions against radiation and convection. In practice, a single spark from an induction coil often takes the place of more clumsy methods of raising the temperature. The heat *produced by the interaction itself*, however, is fixed in amount, and depends only on the materials and their quantity.

Heating is not the only means used to give the initial acceleration to a self-sustaining chemical change. The materials in a match-head are capable of undergoing a great transformation. Yet, so slowly does this proceed at ordinary temperatures, that matches may be kept in efficient condition for years. Here a rather violent vibration is employed to hasten the torpid action in a small part of the material, and the heat produced by the resulting action quickly ignites the whole.

The misleading term, **kindling temperature**, is often used in this connection. It gives the impression that there is a definite temperature at which combustion will start. But the temperature is only *one* of the conditions which produce combustion. Finely powdered iron will start burning at a lower temperature than will an iron wire, *because it presents relatively more surface to the gas*. Finely divided lead, known as "lead pyrophorus," catches fire at room temperature. Again, if the oxygen is at less than one atmosphere pressure, the wire will require to reach a higher temperature before combustion will begin. Finally, the vapor of methyl alcohol and air requires to be raised above a red heat before combustion starts, but a pocket cigar-lighter sets fire to this very mixture by means of a *contact agent* (a thin platinum wire) without any other means of heating being required. So that, the conditions under which combustion begins involve the physical condition of the solid, the pressure of the gas or vapor, the presence or absence of a contact agent and the nature of the contact agent, as well as the temperature. No definite kindling temperature can be given, unless the other conditions are specified also. **Kindling conditions** involve several variables, of which the temperature is only one.

**Spontaneous Combustion.** — Sometimes a mere slow oxidation develops into a combustion, which is then known as **spontaneous combustion**. To understand this, we must note the fact that a given weight of material, say, iron, in combining with oxygen to form a given oxide, will liberate the same total amount of heat whether the union proceeds rapidly or slowly. If the action proceeds slowly, and the material being oxidized is freely exposed to the air, the lat-

ter will become heated and will carry off the heat as fast as it is produced. Thus, no particular rise in temperature will occur. If, however, the material is a poor conductor of heat, like hay or rags, and there is sufficient air for oxidation, but not enough to carry off the heat, the heat may accumulate and a temperature sufficient to start combustion may be reached. Such a situation sometimes arises in hay-stacks. It occurs also when rags, saturated with oils used in making paints (linseed oil and turpentine), are left in a heap. These oils, in "drying," combine with oxygen from the air and turn into a tough, resinous material. The rags, being poor conductors of heat, finally become hot enough to burst into flame, and serious conflagrations often owe their origin to causes such as this. Oily rags should always be disposed of by burning, or should at least be placed in a closed can of metal. Fires in coal bunkers of ships arise from the same cause, slow oxidation (p. 93), with accumulation of the resulting heat.

***Other Means of Altering the Speed of a Given Chemical Change: By Change in Concentration; by Catalysis; by Solution.***— Even when the temperature remains constant, there are other changes in the conditions (p. 41) which may be used for accelerating or for moderating the speed of chemical interactions. The most important of these is, a change in the **concentration** of the interacting substances. Another is the presence of a **catalytic** or **contact agent**. The condition of **solution** might be accounted still another.

The abatement in the activity of the oxygen found in the air (p. 94), by the nitrogen which is mixed with it, is a question of concentration. If the concentration of pure oxygen under atmospheric pressure is taken as unity, that of oxygen in air is only about 0.2. And the speed of interaction of a body, other things being equal, is directly proportional to its concentration. This is not an obscure law, but merely common sense put into definite language. The *opportunity* which one substance has for getting at every part of another will be one factor in determining the speed with which the resulting transformation will take place. And this opportunity, other things being equal, depends on the thickness or density with which the substance is scattered in the region of action. In the case of a gas, this factor is measured by its partial pressure. Hence, lights burn badly at great elevations, where the oxygen is very tenuous. On the other hand, powdered charcoal, which burns feebly

in common air, interacts so rapidly when ignited in liquid air, where the oxygen is highly condensed, that an explosion takes place. Again, when oxygen is compressed in contact with barium oxide at  $700^{\circ}$  it combines to form the dioxide (p. 82); when the pressure of the oxygen in contact with the latter is reduced, oxygen is liberated (see Chemical equilibrium).

When, without any change in temperature, an extra substance increases the speed of a chemical change, seemingly by its mere presence, without itself suffering any permanent change, we call this **catalytic** (Gk. *κατά*, down, *λύσις*, the act of loosing) or **contact action**. The word was originally used for cases of decomposition.

The foreign body is called the catalytic or contact agent, and the process catalysis.

The effect of manganese dioxide on the decomposition of potassium chlorate (p. 83) is of this nature. When some of the chlorate is placed in a flask, provided with a two-hole stopper and exit tube, and is melted carefully so as to avoid superheating, scarcely any evolution of oxygen can be perceived at this temperature ( $351^{\circ}$ ).

If now a pinch of pulverized manganese dioxide, hitherto held in the closed tube, be dropped into the molten mass by turning the end of the tube into a vertical position (Fig. 32), the oxygen is given off in torrents in consequence of the enormous acceleration of the decomposition. To avoid injury from an explosion, it is advisable to wrap the flask in a towel, before turning the tube. Yet the manganese dioxide may be recovered unchanged from the residue. Manganese dioxide, of course, will itself give oxygen (p. 82), but the decomposition is hardly noticeable at  $400^{\circ}$ . Oxone (p. 85) always contains a trace of cuprous hydroxide, which hastens the action on water.

It is found that many actions owe what appears to be their normal speed to the presence of a trace of water vapor. Thus many of the elements show no visible tendency to unite with carefully dried oxygen, even when they are strongly heated in it. Addition of a trace of moisture, however, brings about instant combustion. So water is to be regarded as one of the commonest contact agents.

A few cases of retardation of an action by a catalytic agent are known. Thus a little benzyl alcohol or mannite added to the solution will retard the oxidation of sulphites by the air (Bigelow). Hence positive and negative catalysis both occur.

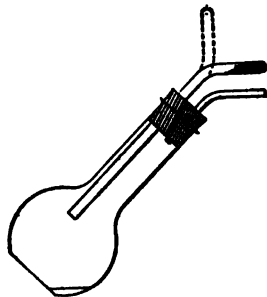


FIG. 32.



The effect of **solution** in hastening a chemical change was seen when we examined the interaction of sodium chloride and silver nitrate (p. 19). With the solutions the action was seemingly instantaneous. If we had attempted to bring it about by rubbing the dry substances in a mortar, hours of work would have left much of the original bodies still unchanged. Even heating would not have produced so prompt an effect. It is obvious that the intimate access which every part of each solution gains to every part of the other accounts to some extent for the difference (see Ionization). Chemical actions, as will be seen in the sequel, are very frequently carried out in aqueous solution in order to take advantage of the favorable influence of this condition.

**Thermochemistry.\*** — As we have seen (p. 28) a chemical change may be accompanied either by a liberation or an absorption of heat. Actions, like the oxidations in the present chapter, in which heat is produced, are called **exothermal** actions. Actions which, like the decomposition of mercuric oxide (p. 17), or of barium dioxide (p. 82), absorb heat, and proceed only so long as heat is furnished, are called **endothermal** actions. Since the activities, or affinities of two substances (say, two metals) may often be measured (p. 37) by observing the amounts of heat liberated when each combines with a third substance (say, oxygen), it will be instructive now to consider some of the elementary facts of thermochemistry.

The chemical interactions to be studied thermally are arranged so that they may be carried out in some small vessel which can be placed inside another containing water. The whole apparatus is called a **calorimeter**. The heat developed raises the temperature of the water. Where gases, like oxygen, are concerned, a closed bulb of platinum forms the inner vessel. The quantity of heat capable of raising one gram of water one degree in temperature, at 15°, is called a **calorie**. So that 250 grams of water raised 1° would represent 250 calories, and 20 grams of water raised 5° would represent 100 calories.

While in physics the unit of quantity is the gram, in chemistry the unit which we select is naturally that represented by the formula of the substance. Thus, the heat of combustion of carbon means the heat produced by combining twelve grams of carbon (charcoal)

\* This section may be omitted at this point, and can be taken up very appropriately in connection with fuels, under carbon.

with thirty-two grams of oxygen, and is sufficient to raise 97,600 grams of water one degree. This is expressed as follows:



In other words, the combustion of less than half an ounce of carbon will raise one kilogram (over two pounds) of water from 0° almost to the boiling-point.

It is always found that the same quantities of any given chemical substances, sustaining the same chemical change under the same conditions, produce or absorb, according as the action is exothermal or endothermal, amounts of heat which are equal.

The *rate* at which a given chemical action is allowed to take place has no influence on the total amount of heat consumed or produced. It may not at first sight appear obvious that rusting evolves heat, but a delicate thermometer will show that a heap of rusting nails is somewhat higher in temperature than surrounding bodies. As we have seen (p. 96), poor conductors, like oily rags and ill-dried hay, show a tendency to spontaneous combustion owing to accumulation of the slowly developing heat of oxidation; and the warmth of our own bodies is due to the same cause.

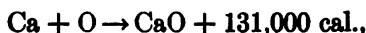
In accordance with invariable experience expressed in the law of the conservation of energy, when an action is chemically capable of reversal, the contribution of the same amount of heat which it develops will exactly suffice to drive the chemical change in the opposite direction. The heat contributed is simply used to restore the amount of chemical energy proper to the original system. Thus, the union of one chemical unit weight each of mercury and oxygen (p. 80) produces 30,600 cal.:



and the decomposition of one formula-weight of mercuric oxide (p. 17) demands the same amount of heat in order that free mercury and oxygen, with their appropriate proportions of internal energy, may be recovered.

In practice it is found that all chemical changes are not capable of reversal by the use of the sources of heat available in the laboratory. A quantity of heat, equivalent to that produced by any chemical action on a small scale, is very easily provided, but something more appears to be necessary. The heat provided must be of a certain *temperature*, otherwise it is quite ineffective. For example, the heat

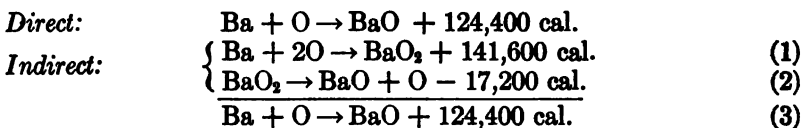
produced by the union of calcium and oxygen is within the limits of ready measurement,



and the supply of this amount (or even of unlimited amounts) of heat to calcium oxide (quicklime) is easily achieved. Yet this method is quite ineffective to produce decomposition (p. 23) of the product. Apparently we have not sufficiently high temperatures for the purpose at our command (see Factors of energy).

It may be noted in this connection that the temperatures required to produce reasonably rapid decomposition vary within a wide range. Some substances can be kept only below  $0^\circ$ , and decompose when allowed to become warm. Others, like the oxides of gold and platinum, require a little heating (p. 122). Many, like quicklime, are not broken up even at the temperature of the electric arc. When the energy is applied in the form of electricity (p. 28), instead of heat, the range is incomparably more easily within the reach of the means ordinarily at our disposal. There is no substance, provided it is of such a nature as to be affected by the electric current at all, which cannot be decomposed by a current with an E.M.F. of 10 volts or less, while currents of 110 volts and over are commonly accessible. It is partly on this account that electrical processes have become so common in industrial chemistry.

One of the most important principles of thermochemistry is the law of constant heat summation. If a system of substances can be transformed into another system of substances by different stages or by more than one route, then the algebraic sum of the heats absorbed or produced in the various routes is the same. Thus, barium oxide might be formed either *directly* from the proper proportions of the constituents, or *indirectly* by preparing the dioxide (p. 82), and then driving out half of the oxygen contained in the latter. The quantities of heat involved in these two routes are as follows:



When equations (1) and (2) are added algebraically, canceling terms such as  $\text{BaO}_2$  and  $\text{O}$ , which are common to both sides of the final equation, the fact that the indirect route is exactly equivalent to the direct one is at once apparent, and the balance, in favor of heat produced, is 124,400 calories as before. If in such cases the sum

of the heats were not the same, it would follow that by using different plans of procedure we could prepare different specimens of the same substance containing different proportions of chemical energy. This, however, we have never been able to do.

The quantities of heat liberated in two chemical changes are often measures of the relative amounts of available chemical energy in the systems before the change, and, therefore, often furnish a measure of the relative chemical activities of the two sets of substances. The comparison may safely be made in certain cases when the conditions under which the two actions take place are precisely alike. Formerly it was supposed that the heat liberated was always proportional to the chemical activity of the substances, but we have already shown cause (pp. 35, 37) why this general statement cannot be true.

It should be noted that production or absorption of heat is not, in itself, an evidence of chemical action. Physical changes are likewise accompanied by the same phenomena. Thus, the evaporation of water absorbs heat, and condensation of a vapor and the crystallization of a supercooled liquid liberate heat.

**Exercises.\*** — 1. Enumerate other instances, already encountered, of the use of the terminations *ous* and *ic* to distinguish different degrees of oxidation. For what other purposes have the same terminations been used?

2. What difference in composition between potassium chloride and chlorate are the terminations designed to indicate? Applying the same idea, how would ferrous sulphate (*q.v.*) differ from ferrous sulphide, and cupric sulphate from cupric sulphide?

3. Define and illustrate: density of a gas (p. 86, and see p. 111), density of a solid or liquid (pp. 3, 86).

4. Enumerate the classes of facts given under the heads of, Physical Properties, and Chemical Properties of oxygen, respectively.

5. Construct the equations for the combustion of phosphorus, carbon, and iron in oxygen (pp. 90, 91).

6. What weight of oxygen may be obtained by heating 30 g. of barium dioxide (p. 82)? In solving this problem, pay minute attention to the rules (p. 75).

7. When 1 g. of sodium burns in oxygen, it produces 1.7 g. of the oxide. What is the formula of the latter, and the equation (p. 72)?

8. How should you show that, in the making of oxygen from a mixture of potassium chlorate and manganese dioxide, the latter

\* See footnote to p. 26.

remains unchanged? Which properties (p. 40) are you employing for this purpose?

9. The substances, like phosphorus and sulphur, which burn rapidly in ordinary oxygen, combine very, very slowly (even when heated) with oxygen which has been freed from moisture by careful drying. How is this effect of water to be classified?

10. Discuss the union of iron and sulphur (p. 16) and the decomposition of mercuric oxide (p. 17) in their relation to the explanations on pp. 94-95.

11. How many calories are required to raise 500 g. of a substance of specific heat 0.5 from  $15^{\circ}$  to  $37^{\circ}$  (p. 98)?

12. The combustion of 1 g. of sulphur to sulphur dioxide develops 2220 calories. What is the heat of combustion of sulphur (p. 99)?

13. Outline briefly the proof that thermochemical data are not accurate measures of chemical activity (p. 35).

14. What percentage by weight of free oxygen is obtained by heating: (a) mercuric oxide, (b) potassium nitrate, (c) potassium chlorate? At \$1.50 (7/8), \$0.15 (8d), and \$0.15 (8d) per kilogram, respectively, which is the cheapest source of oxygen?

15. Using the data on p. 86, calculate the weight of oxygen dissolved by 100 c.c. (= 100 g.) of water at  $20^{\circ}$ .

16. Why does a forced draft make a fire burn more rapidly?

17. Why does a naked flame sometimes cause an explosion in a mine, when the air of the mine is filled with coal dust?

18. When iron wire burns in oxygen, the oxide of iron falls in melted globules, and no smoke is produced, while when phosphorus is burned, all the oxide goes off as smoke, and nothing remains in the spoon. Explain this difference.

## CHAPTER VI

### THE MEASUREMENT OF QUANTITY IN GASES

WE have spoken of measuring the proportion by weight of the oxygen used in several chemical changes, but in our illustrations we have never weighed the gas itself. We have always (*e.g.*, p. 90) obtained its quantity by subtracting the weights of solid or liquid bodies. In practice this method often serves the purpose.

Our preference for weighing as a means of ascertaining quantity of matter is largely due to the fact that the weight is independent of the physical or even chemical condition of the substance. Yet, with proper precautions, we may learn the quantity of matter by means of any other attributes which are proportional to it. Now the volume is such an attribute. In determining the quantity of a liquid, where rapidity with no extreme accuracy is desired, the volume is frequently measured. In the case of gases the error made in measuring the volume is less, as a rule, than in measuring the weight.

***The Variable Concentration of Gases.*** — A little experience with gases soon shows us that measurement of volume alone does not necessarily give any definite idea of the quantity of matter present. The denseness with which the gaseous matter is packed (the **concentration** of the gas) in the vessel must somehow be defined, as well as its volume, in order that there may be specification of the quantity of matter.

Gases vary markedly in chemical activity with changes in their concentration (*cf.* p. 94), and thus the consideration of this condition (p. 41) is continually forced upon the chemist. Solids and liquids do not alter their denseness of packing (concentration) very noticeably even when compressed severely or changed in temperature. So that concentration need not be considered in the case of pure bodies in the solid or liquid forms. Such substances can be scattered through a variable space by solution in some solvent, however, and then their degree of packing or concentration becomes an important factor in *their* chemical behavior also.

The principle used for estimating the concentration of a gas may be illustrated by means of the arrangement in Fig. 33. Except that

a little gas (any gas will do) remains shut off by the mercury in the left limb of the tube, the whole apparatus has been evacuated. The reservoir can be turned upward, and thus larger amounts of mercury may be introduced into the tube.

Now the portion of the mercury below the dotted line is essentially a balance, that is to say, it will move in one direction or the other if the stresses on either side change. At present these stresses must be equal. On the right pan of the balance, so to speak, the stress is represented by the weight of the column of mercury above the dotted line. As there is nothing in the tube above this mercury, the weight of the latter is all that this side of the balance sustains. On the left pan of the balance there must be an equal stress, and this stress can be caused only by the gas confined in the shorter limb. The nature of a gas suggests that this stress must be exercised on the walls of the tube also, although they naturally do not exhibit its effects. This stress we call the **pressure of the gas**.

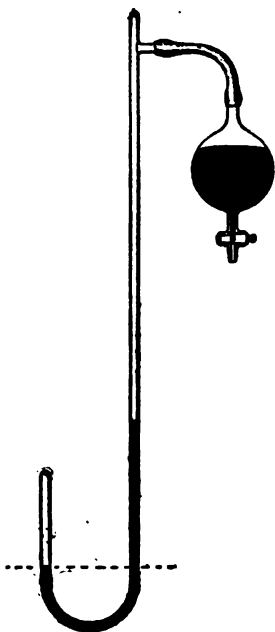


FIG. 33.

The height of the surface of the mercury on the right above that on the left having been measured, more mercury may now be added from the reservoir, and the difference in the two levels again noted. The gas cannot have diminished in amount, yet it now occupies a smaller space, and is, therefore, packed more closely — its concentration is greater than before. If, for example, the difference in level is now twice as great, it will be found that the concentration of the gas is also twice as great (its volume having become half of the original volume). Whatever amount of mercury is added, we shall always find that the concentration of the gas is proportional to the height of the mercury. But this in turn is proportional to the weight of metal. The weight of mercury on one side must, therefore, be equal to the stress or pressure or tension of the gas on the other side which balances it. Hence, the concentrations of a sample of any gas are proportional to the corresponding pressures it exercises. We determine, therefore,

the denseness with which any sample of gas is packed by measuring its pressure.

**Method of Allowing for Varying Concentration in Measuring Quantity in Gases.**—The principle just stated is applied to the measurement of the quantity of matter in a sample of gas by permitting the concentration of the sample to alter until it is equal to that of the atmosphere at the moment. Then we read off the volume now occupied, and simultaneously we ascertain the pressure by observing that of the atmosphere. Each of these two operations is facilitated by a special arrangement of apparatus.

A gas to be measured is always confined so that some liquid constitutes one part of the barrier to its escape. The very simplest form of the apparatus is shown in Fig. 34. To render the concentration (and pressure) of the gas equal to that of the atmosphere, the cylinder containing the gas is lowered (or raised) until the levels of the liquid inside and outside are the same. When the system is in this condition the stress of the gas on the inner surface must be equal to that of the atmosphere on the outer one, otherwise movement of the liquid would occur. The volume of the gas is then read directly from the graduation on the cylinder. Often the cylinder, or other vessel, is closed with a ground-glass plate, placed quickly in erect position, and weighed. The weight of water which is then required to fill it to the brim gives more exactly the volume occupied by the gas (1 g. water = 1 c.c.). When special modes of admitting or handling the gas have to be provided for, the apparatus may be more complex. But the principle of adjustment is always the same. In exact work, mercury is employed to confine the gas. Water serves the purpose of rough work with gases which, like oxygen, are but slightly soluble in it. When water is used, the volume is too great by the space occupied by the vapor of the water which is mixed with the gas (see Mixed gases, p. 111), and a correction must always be made on this account.

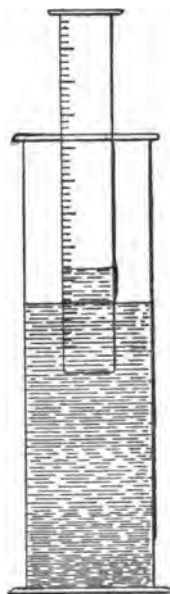


FIG. 34.

The pressure or tension of the atmosphere at any moment is measured by means of a simplified form of the apparatus in Fig. 33.



The reservoir is omitted, but the space above the mercury on the right is still a vacuum. The atmospheric air being the gas whose concentration is to be measured through its pressure, the short limb is left open. The resulting apparatus (Fig. 35) performs its functions in the same way as does the more complex one. The only difference

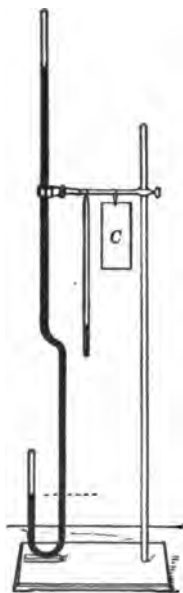


FIG. 35.

is that mercury is *automatically* added to or withdrawn from the right side by the motion of the metal resulting from changes in the pressure of the air. The reading of the vertical height between the lower and upper surfaces of the mercury gives a number which is proportional to the weight of mercury on the right side of the balance and, therefore, to the (equal) stress of the atmosphere on the left. This is called the *barometric reading* (uncorrected), after the name of the instrument.

To make different readings, taken when the mercury is at different temperatures, strictly proportional to the weight of the metal, the observed height is always *reduced* to that which would have been shown by the same weight of mercury at  $0^{\circ}$  in the same apparatus. A thermometer, and a table of temperatures with the corresponding corrections to be subtracted from the uncorrected reading (*C*, Fig. 35), must be used.

Knowing now the volume occupied by the sample of gas when its concentration is equal to that of the atmosphere and the barometric reading, which is proportional to this concentration, the measurement of the amount of matter in the sample has become definite so far as concerns the variability of concentration with change in pressure.

**Boyle's Law.** — The recorded results of measurements made as above at different times, when the atmospheric pressures are different, are still unsatisfactory because the data for samples of the same kind of gas differ in the value of the pressure as well as in that of the volume. To make the results easily comparable in respect to the amount of matter they represent, one further step is needed. All the data are recalculated so as to show the volume each sample would have occupied if the pressure had been equal to the weight of 760 mm. of mercury, which is the average height of the barometer at the sea level in  $45^{\circ}$  of latitude.

We have seen that the concentration of a given quantity of a gas is proportional to its pressure (p. 104). But, volume occupied is the inverse of concentration. Thus, the same rule may be stated in the form: **The volumes occupied by a sample of any gas are inversely proportional to the pressure at each volume.** The fact was discovered by Boyle (1660) who stated it in this way. In still other words, the product of the several pressures and corresponding volumes of a sample of gas is a constant.

A numerical illustration will show the mode of applying this rule. We measure 200 c.c. of a gas at atmospheric pressure, and the barometer reads 742 mm. The question is: What would be the volume of this amount of gas at 760 mm. barometric pressure? It will be  $200 \times \frac{742}{760}$  c.c. = volume at 760 mm. It is unnecessary to use any formula, but absolutely essential to ask: Is the new pressure greater or less than the old? Here it is *greater*. Hence, according to the law, the new volume will be *less*, so that the fraction must be arranged with the smaller number in the numerator.

Boyle's law may be illustrated by using a long tube bent like a barometer (Fig. 35) but having the short limb closed and the long one open. Strips of paper mark the levels of the mercury, which are at first alike on both sides, and register the volume of the air in the short limb at a pressure of one atmosphere. The reading of the barometer at the time, say 750 mm., is noted. Then mercury is added through a funnel inserted in the long limb, until the level in this limb is 750 mm. above that in the other. A stick cut to 750 mm. length, and held beside the tube, will conveniently show when this has been accomplished. The pressure in the open limb being now two atmospheres, the volume of the air will be found to have diminished to one-half its former value.

For pressures lower than one atmosphere, a different arrangement must be used. A graduated tube, closed at one end, is partly filled with mercury and inverted in a tall, narrow cylinder full of the same metal. The tube is then clamped in any position, such that the mercury level in the tube is above that in the cylinder. The reading of the barometer is next noted. The volume occupied by the air in the tube is then read, and the difference in height of the two mercury surfaces is measured by means of a graduated rule. Subtracting this height from that of the barometer gives the pressure of the air in the tube. The position of the tube is then altered, and the same measurements repeated, as often as is wished. The product of each volume and the corresponding pressure will be a constant number. The law is expressed mathematically by letting  $p_1$  and  $v_1$  represent the initial pressure and volume,  $p_2$  and  $v_2$  the new pressure and volume, and so forth. Then  $p_1 v_1 = p_2 v_2 = \text{constant}$  for that particular specimen of gas. For a given sample of gas, any one of the four values may be calculated if the other three are known.

Boyle's law states the facts with sufficient accuracy for all ordinary purposes. But in reality no two gases behave *precisely* alike in respect to change in concentration when the pressure is altered (see Chap. IX). The same gas does not even behave in precisely the same way at high, intermediate, and low pressures. The ideal gas, which should behave uniformly, we call the *perfect* gas. With most gases, at low pressures concentration increases more, and at very high pressures much less than the rule indicates (see Kinetic theory).

***The Relation of the Volume of a Gas to Temperature.***—

In the foregoing we have assumed that there were no temperature effects. But, as a matter of fact, a rise in temperature will at once produce an increase, and a fall in temperature a decrease in the pressure of an enclosed sample of a gas. Hence a record of the pressure alone will fail to indicate the concentration definitely, and volume and pressure together will still leave the amount of material unspecified. The temperature must, therefore, be given as well.

Our descriptions of different samples of gas, at different temperatures, having thus become once more incomparable, we apply the same kind of remedy as before. We calculate the volume which each specimen of gas would occupy at  $0^{\circ}$ .



FIG. 36.

The rule for this calculation may be demonstrated in a rough way as follows: The large, graduated bulb (Fig. 36) is surrounded by a vessel which can subsequently be filled with ice water or with water of any temperature up to  $100^{\circ}$ . About one-half of the bulb is occupied by the gas. The mercury which fills the rest is connected with a reservoir, so that the levels of the metal can be made alike, and the pressure of the gas be maintained constantly the same as that of the atmosphere. When, now, the volume occupied by the gas at  $0^{\circ}$  is read, and warmer water is introduced, we find that the volume gains  $\frac{1}{273}$  of its value at  $0^{\circ}$  for every degree through which its temperature rises. If it is cooled below  $0^{\circ}$ , it loses  $\frac{1}{273}$  of its volume at  $0^{\circ}$  for every degree through which the temperature is lowered. Observation gives practically the same value for all gases.

The following graphic method will put these facts in a clearer light. In Fig. 37 we have on the left a thermometer scale divided into degrees Centigrade. The middle line represents the volumes of a given sample of gas which correspond with the successive tem-

peratures. If we, for convenience, take a volume of 273 c.c. of a gas at  $0^{\circ}$  and warm this through  $1^{\circ}$ , then at  $1^{\circ}$  its volume, having gained  $\frac{1}{273}$  of its original value, becomes 274 c.c. At  $2^{\circ}$  it has gained another  $\frac{1}{273}$  of the volume it had at  $0^{\circ}$  and becomes therefore 275 c.c., etc. If cooled below  $0^{\circ}$  it loses  $\frac{1}{273}$  of the volume, becoming 272 c.c., etc.

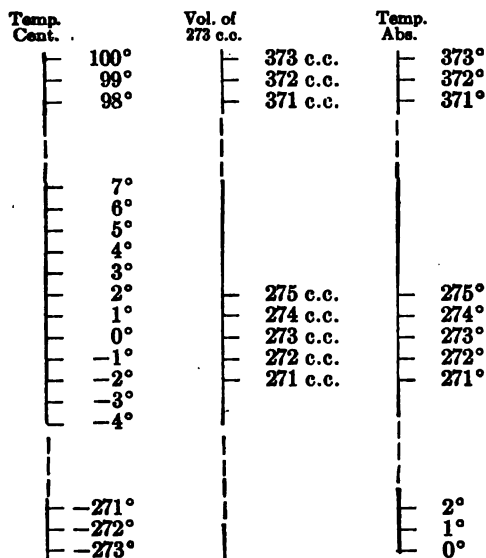


FIG. 37.

If the gas be heated to  $100^{\circ}$  it gains  $\frac{1}{273}$  of its volume at  $0^{\circ}$  and becomes 373 c.c. We might infer that if it were cooled through  $273^{\circ}$  from  $0^{\circ}$  it would lose  $\frac{1}{273}$  of its volume, in other words, it would disappear. This temperature has not yet been reached, and in any case all gases would presumably liquefy before reaching it. Our statements apply to ordinary temperatures only, and within them the law holds with considerable strictness. Now the series of numbers on the middle line (Fig. 37) are all 273 units larger than the temperatures Centigrade in the line to the left of the figure. If we alter the graduation of the Centigrade thermometer by adding 273 to each temperature, we secure the scale on the right, which exhibits degrees of the very same length as before, but has the additional advantage that the numbers expressing temperature are the same as

those expressing volume. This is what we call the **absolute scale of temperature**. In this artificial case we started with 273 c.c. at  $0^{\circ}\text{C}$ . ( $273^{\circ}\text{Abs.}$ ), and the absolute temperature is here always numerically equal to the volume. If a different volume had been taken at  $0^{\circ}$ , then the volume assumed by the gas at each temperature would have borne a constant ratio to the volumes recorded. Hence, the volumes assumed by a sample of gas at different temperatures, the pressure remaining constant, are in the same proportion as the corresponding absolute temperatures. This is the modern way of stating a fact which was first discovered by Charles of Paris (1787). Obviously, if the *volume* remains constant, then the *pressure* will be proportional to the absolute temperature. The bare fact underlying our statement of the law is that **all gases suffer equal increments (or decrements) in volume (or pressure) for equal changes in temperature**.

The discovery of this fact is generally attributed to Dalton, who first published an investigation of the subject, embodying this result, in 1801, or to Gay-Lussac, who made a more complete investigation in 1802. Inasmuch, however, as in Chemistry we have another important principle known as Gay-Lussac's law, and several which are connected with the name of Dalton, it is on the whole fortunate that we are justified in attributing this discovery to Charles.

The application of this law may best be illustrated by an example. We obtain 200 c.c. of a gas at  $17^{\circ}$  and wish to know what volume it would occupy at  $0^{\circ}$ . To answer the question, we convert the Centigrade temperatures to the absolute scale by adding, algebraically, 273 to each. Thus  $200 \times \frac{273}{350} =$  the volume at  $0^{\circ}$  required. No formula is needed. We simply ask whether the new temperature is higher or lower than the old one. Here it is *lower*. The new volume will therefore be *smaller* than the old one. So we take care to place the smaller number in the numerator.

The law may be put in mathematical form. It is preferable, however, that beginners should use the method employed in the illustration given in the preceding paragraph. Simple mathematical expressions, like the one representing this law, are not made to save us the trouble of remembering the law itself, and it would be unfortunate if their use led us to forget it.

The behaviors of gases in respect to changes of temperature and pressure are perfectly independent of one another, so that the above laws may be applied to any example, either in succession, using the answer for the first calculation in making the second, or simultaneously. Thus 200 c.c. of gas at 742 mm. pressure and  $17^{\circ}$  become  $200 \times \frac{273}{350} \times \frac{760}{742} = 183.8$  c.c. at  $0^{\circ}$  and 760 mm.

**Mixed Gases.**—Two gases at the same temperature, provided they do not interact chemically, do not interfere with each other's pressures when mixed. Thus, if they are forced into the same volume, the pressure of the mixture is equal to the sum of those of the components (Dalton's law, 1807). The gases are therefore still thought of individually, and the share which each gas has in the total pressure is called its **partial pressure**. This, like any other gaseous pressure, is proportional to the concentration of the particular gas in the mixture.

For example, a gas measured over water contains water vapor. The partial pressure of this, called the **aqueous tension**, which is definite for each temperature, must be subtracted from the total pressure. The remainder is the partial pressure of the gas being measured, and this remainder is used as the pressure of this gas in any calculation. Thus, in a gas measured over water at 22°, the total pressure includes 19.7 mm. pressure of water vapor (see Appendix IV). Hence 150 c.c. of gas over water at 22° and 750 mm. is the same amount as 150 c.c. of the same gas in dry condition at 22° and 730.3 mm., there being simply 150 c.c. of water vapor at 19.7 mm. mixed with it. To obtain the volume of dry gas at 0° and 760 mm., we have the expression  $150 \times \frac{273}{295} \times \frac{730.3}{760}$ .

**Densities of Gases.**—The application of the laws of Boyle and Charles enables us to express the quantities of matter in samples of gases in a definite and readily comparable manner. In describing chemical changes, however, it is continually necessary to express quantities of gases by weight. The relation between volume and weight for each kind of gas must, therefore, be ascertained. If we know, for example, the weight of one liter of each gas at 0° and 760 mm. pressure, conversion to other weights, volumes, temperatures, and pressures can be made. The one-thousandth part of this value, the **weight of 1 c.c.**, is called the **density** of the gas. Often, however, the relative weights of equal volumes, with that of air or hydrogen as unity, receive this name.

For most chemical purposes a high degree of accuracy is not required. The most direct method is to employ a light flask of 125–150 c.c. capacity, provided with a rubber stopper and stopcock (Fig. 38). By means of an air-pump the contents of the flask are removed, and



Fig. 38.

it is weighed. This gives the weight of the empty vessel. The gas, whose density is to be ascertained, is then admitted, and care is taken that it finally fills the flask at the pressure of the atmosphere. The flask is closed and weighed again. The increase represents the weight of the gas. At the same time the temperature and barometric pressure are read. The volume is determined by displacing the gas once more from the flask, filling with water, and weighing again. The difference in weight between the empty flask and the flask full of water, in grams, represents the volume of the content of the flask in cubic centimeters. This volume is reduced to  $0^{\circ}$  and 760 mm. by the rules discussed above, and we have then a volume of the gas and the corresponding weight.

To illustrate, let us suppose that the volume of the flask is 200 c.c. and that it is filled with oxygen at  $17^{\circ}$  and 742 mm. The weight of the gas is found to be 0.26 g. We ascertained (p. 110) by calculation that at  $0^{\circ}$  and 760 mm. this volume would be 183.8 c.c. The weight of a liter is given by the proportion  $183.8 : 0.26 :: 1000 : x$ . Here  $x = 1.415$  g. When the operation is performed carefully, and the weighing carried to the nearest milligram instead of the nearest centigram, a result more nearly approaching the exact one (1.429) may easily be reached.

To get the density of oxygen referred to hydrogen as unity, we must divide the answer by the weight of a liter of hydrogen (0.08987 g.). In the above case the quotient is 15.74. The accepted value is 15.90. The density referred to air as unity is similarly obtained by dividing by 1.293, the weight of a liter of air at  $0^{\circ}$  and 760 mm. pressure.

If a suitable pump is not available, the flask, in this case provided with two openings, is weighed without preliminary exhaustion. This gives the weight of the vessel *plus that of the air it contains*. A continuous stream of the gas is then passed into the flask until the air has been completely displaced. The vessel is then closed and another weighing made. Finally the gas is displaced by water, and a third weighing taken. The temperature and barometric pressure are noted as usual. The last weighing gives the volume as before. Knowing that one liter of air weighs 1.293 g. at  $0^{\circ}$  and 760 mm., we may calculate readily the weight of the air which the flask contained at the observed temperature and pressure. When this is subtracted from the number obtained in the first weighing, we have the weight of the empty flask. Subtracting this in turn from a second weighing, we have the weight of the gas. We obtain thus the weight of a known volume of the gas at a known temperature and pressure, and finish the calculation as before.

The values of the densities of gases are of great significance in the chemical point of view. A number of them are given in connection with the discussion of molar weights (*q.v.*).

**Vapor Densities of Liquids and Solids.**—The densities of vapors are as important to the chemist as those of gases and, solids and liquids being more numerous, are even more frequently measured.

A modification of the flask just described is used. A temperature sufficiently high to vaporize the substance must be employed. The volume is reduced by rule to  $0^{\circ}$  and 760 mm., and the density, in this case known as the **vapor density** (wt. of 1 c.c.) is calculated as before. The reduction to  $0^{\circ}$  and 760 mm. pressure by rule gives, of course, a fictitious result. The vapor would condense to the liquid form before  $0^{\circ}$  was reached, if the cooling were actually carried out. But the value for the density *as it would be* at  $0^{\circ}$  and 760 mm. has to be calculated to facilitate comparison with the corresponding values for other substances. The results have no physical significance, but are highly important to the chemist.

**Exercises.**—The foregoing cannot be understood unless some problems involving the laws of gases are actually worked.

1. Reduce 189 c.c. of gas at  $15^{\circ}$  and 750 mm. to  $0^{\circ}$  and 760 mm.
2. Reduce 110 c.c. of gas at  $-5^{\circ}$  and 741 mm. to  $0^{\circ}$  and 760 mm.
3. Convert 500 c.c. of gas at  $25^{\circ}$  and 700 mm. to  $18^{\circ}$  and 745 mm.
4. Reduce 250 c.c. of gas, standing over water, at  $21^{\circ}$  and 765 mm., to the dry condition and to  $0^{\circ}$  and 760 mm.
5. An evacuated bulb weighs 13.312 g. After being filled with the vapor of carbon tetrachloride at  $100^{\circ}$ , it weighs 13.951 g. Filled with water it weighs 141.3 g. The barometric reading (corr.) is 755 mm. What is the vapor density?
6. The density of a substance referred to air is 3.2. What is the density referred to hydrogen? What will be the volume occupied by 10 g. of the substance at  $20^{\circ}$  and 752 mm.?



## CHAPTER VII

### HYDROGEN

**HYDROGEN**, although discovered by Paracelsus in the sixteenth century, was confused with other combustible gases, and its independent nature was first established by Cavendish in 1766. Somewhat later (1781), the latter showed that hydrogen when it burned in the air gave water vapor, of which he condensed a large quantity to the liquid form. Taken in conjunction with Lavoisier's proof that oxygen was the active substance in the air (1777), this fact showed that water was a compound of hydrogen (Gk. ὕδωρ, water; γέννᾶν, to produce) and oxygen, and not a simple substance.

**Occurrence.** — The free element is found, mixed with varying proportions of other gases, in exhalations from volcanoes, in pockets found in certain layers of the rock-salt deposits, and in some meteorites. The air contains not more than one part of it in 1,500,000. Its lines are very prominent in the spectra of the sun and of most stars.

In combination, it constitutes about 11 per cent of water. It is an essential constituent of *all* acids. It is contained also, in combination with carbon, in the components of natural gas, petroleum, and all animal and vegetable bodies.

We have seen (p. 24) that, using the physical unit of weight, the element hydrogen stands ninth in order of plentifulness. But the *chemical* work that elements can do should rather be reckoned by the relative numbers of atomic weights which are available. When Clarke's numbers are recalculated to this basis, and the number of chemical unit weights of oxygen is called 100, hydrogen assumes a position more in harmony with its importance:

Oxygen . .	100.00	Aluminium . .	8.63	Iron . . . .	2.37
Hydrogen .	31.13	Sodium . . .	3.25	Calcium . . .	2.53
Silicon . .	29.52	Magnesium . .	2.78	Potassium . .	1.91

**Preparation by the Action of Metals on Cold Water.** — To liberate hydrogen from water, it is necessary to use some element with which the oxygen of the water will combine even more eagerly

than with hydrogen, and to offer this element in exchange for the hydrogen.

The most active metals, such as potassium K, sodium Na, or calcium Ca, displace hydrogen rapidly from cold water. Potassium and sodium are lighter than water, and float on the surface. In the case of the former, so much heat is liberated that the hydrogen catches fire, and with neither metal is the experiment safe in the hands of a novice. Calcium sinks to the bottom, and acts rapidly, but not violently, so that the gas is easily collected (Fig. 39). The pieces of these metals, of course, act upon only a small part of the water in the vessel. In each case the metal displaces one-half only of the hydrogen in that part of the water upon which it acts. The other products are the hydroxides of potassium, sodium, and calcium, respectively. The two former dissolve, leaving a clear liquid when the metal is all gone, but may be recovered as white solids by evaporation. The calcium hydroxide (slaked lime) is dissolved only in part, and much of it may be seen after the action, suspended in the water.

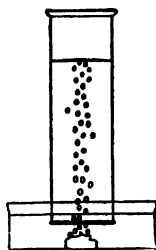


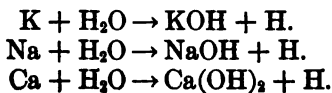
FIG. 39.

An alloy of lead with sodium (35 per cent), sold under the name of **hydrons**, affords a convenient substitute for sodium in the foregoing actions.

**The Making of Equations.** — To make an equation we must have the results of quantitative measurements. These furnish us with the composition of each substance concerned. The composition, expressed in multiples of the atomic weights, is recorded in the formula of the substance. If we are in possession of the necessary formulæ, we can write the equation.

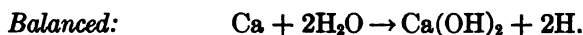
*For example*, the composition of water is: hydrogen  $2 \times 1.008$ , oxygen 16. In symbols, this is  $2H$  and  $O$ , and the formula is therefore  $H_2O$ . The composition of potassium hydroxide is: potassium 39.1, oxygen 16, hydrogen 1.008, and the formula therefore  $KOH$ . In calcium hydroxide the proportions are: calcium 40.07, oxygen  $2 \times 16$ , hydrogen  $2 \times 1.008$  and the formula  $Ca(OH)_2$ .

To make the equation, we first write down the formulæ of the substances used and produced:



*Skeleton:*

Next we must balance the equation, if necessary. That is we must adjust it so that there are equal numbers of atomic weights (or atoms) of each element on both sides of the equation. This is necessary only in the third equation, and is done because, according to the law of conservation of mass, there must be the same quantity of each element after the reaction as there was before it. On examining the third equation, we note there is 2O, in the  $(OH)_2$ , on the right side and only O on the left. We therefore place a 2 in front of the  $H_2O$ , for we cannot get the additional oxygen excepting by using more water:



The number of atomic weights of hydrogen is made equal by using 2H on the right side.

The reader must practice the making of equations, until he can do it quickly. The text contains many equations, but more usually only the data required for making them (the formulæ of the substances) are given.

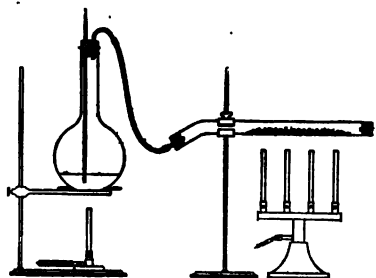
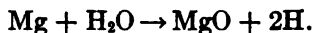


FIG. 40.

### ***Hydrogen from Metals and Water at a High Temperature.***

— With steam at a red heat, metals like iron, zinc, and magnesium, also red-hot, interact vigorously. The steam, generated in a flask, enters at one end of the tube containing the metal

(Fig 40), and the hydrogen passes off at the other. Since, at a red heat, all hydroxides, except those of potassium and sodium, are decomposed into an oxide of the metal and water, as, for example,  $Mg(OH)_2 \rightarrow MgO + H_2O$ , the *oxides* are formed in this case:



Iron gives the magnetic oxide  $Fe_3O_4$ .

***Making Equations, Again.*** — The skeleton equation for the action of iron on steam is:



We are not permitted to alter these formulæ themselves, but we may put coefficients in front of any of them to make the number of

atomic weights alike on both sides. The rule (p. 73) is to *pick out the largest formula* and reason back from that. Here, this is  $\text{Fe}_3\text{O}_4$ . To get  $\text{Fe}_3$ , we must start with  $3\text{Fe}$ , and to get  $\text{O}_4$ , we must start with  $4\text{H}_2\text{O}$ :

*Balanced:*  $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{H}.$

**Acids.** — In making hydrogen in the laboratory, the acids are used almost exclusively. The common acids are hydrochloric acid  $\text{HCl}, \text{Aq}$  and sulphuric acid  $\text{H}_2\text{SO}_4, \text{Aq}$ . The usual forms are mixtures containing water, the variable amount of the latter being indicated by the symbol  $\text{Aq}$ .\* **Hydrochloric acid** is a solution of a gas, hydrogen chloride. The "pure concentrated" hydrochloric acid used in laboratories contains nearly as much of the gas (37 per cent by weight) as the water can dissolve. When heated, it readily gives up part of the gas, and the effervescence attending this must not be mistaken for evidence of chemical action. The "commercial" acid contains impurities and is also less concentrated. The "concentrated," pure **sulphuric acid** is an oily liquid containing practically no water. The "commercial" sulphuric acid contains 6 to 7 per cent of water, besides impurities. **Acetic acid**  $\text{HCO}_2\text{CH}_3, \text{Aq}$  is a solution of a liquid in water.

All the **dilute acids** contain 70 to 80 per cent of water. The water, as a rule, takes no part in the chemical changes in which the acids are concerned, and is therefore omitted from the equations.

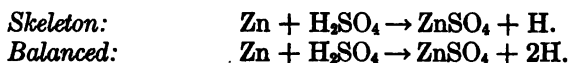
The name **acid** is restricted to one class of substances having certain definite characteristics. Hydrogen is the one essential constituent of all acids. Their aqueous solutions have a sour taste and change the color of litmus, a vegetable coloring matter, from blue to red. When free from water they do not conduct electricity. We shall note presently two other properties which acids show when dissolved in water, namely, that they conduct, and are decomposed by the electric current, and that their hydrogen (or one unit weight of it in the case of acetic acid) is displaced by certain metals.

**Radicals.** — In describing the chemical behavior of acids, we speak of the hydrogen as the **positive radical**, because in electrolysis (p. 28) it is attracted to the negative pole, and of the material combined with the hydrogen as the **negative radical** because it is attracted to the positive pole (see p. 120). Thus the negative radi-

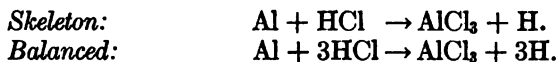
\* See footnote on p. 91.

cals in the above acids are Cl, SO<sub>4</sub>, and CO<sub>2</sub>CH<sub>3</sub>, respectively. The first (Cl) is a simple radical, the others are compound radicals. In many interactions the compound radicals move as units from one state of combination to another.

**Preparation by Displacement from Diluted Acids.** — Every one of the metals which displace (p. 115) hydrogen from water will also displace it from dilute acids. The acids *must be diluted with water*, unless, like hydrochloric acid, they are already dissolved in water. The action is much more vigorous than that on water, so that the most active metals are not employed. Metals like zinc, iron, and aluminium serve the purpose. The metal combines with the negative radical, and so liberates the hydrogen, which escapes in bubbles. Evaporation of the clear liquid, when the metal has all disappeared, gives in dry form the compound of the metal with the negative radical. Thus, with zinc and dilute sulphuric acid, zinc sulphate ZnSO<sub>4</sub> is produced:



With aluminium and hydrochloric acid, the product is aluminium chloride AlCl<sub>3</sub>:



The water undergoes no change during the action, although its presence is essential. It is simply a part of the apparatus. Any acid may be used, although with many the action goes on very slowly.

For preparing small amounts of hydrogen, the apparatus (Fig. 41) is such that additional acid may be added through the thistle, or safety tube. This avoids opening the flask and admitting air. The gas may be caught like oxygen over water or, being lighter than air, may be collected by **downward displacement** of the latter (Fig. 42a). Heavy gases are collected by **upward displacement** of air (Fig. 42b).

With Kipp's apparatus (Fig. 43), the gas may be made on a large scale and its delivery can be regulated. When the stream of gas is shut off by the stopcock, the pressure of the gas, as it continues to be generated, drives the acid away from the metal and up into the globe above, so that the action ceases. Yet the action is ready

to begin again the moment any portion of the stored gas is drawn off for use.

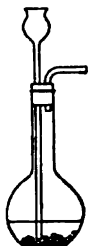


FIG. 41.

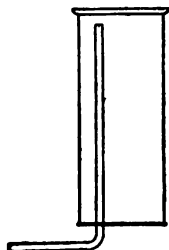


FIG. 42a.

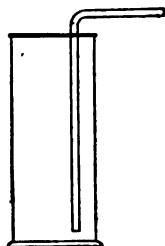


FIG. 42b.

Silver, gold, and platinum, which do not combine with free oxygen, and even copper and mercury, which do, are all *unable* to form oxides and to liberate hydrogen when heated in steam. When treated with dilute acids, *none* of these metals are able to displace and liberate the hydrogen (see Order of activity of the metals, p. 129).

Contact of the zinc or iron with an inactive metal, like platinum or copper, forms an electrical couple (*q.v.*) and hastens the interaction. For the same reason, commercial zinc, which contains traces of other metals, gives a steady evolution of hydrogen, while extremely pure zinc is almost inactive.

When water is *not* used along with the acid, the latter is either inactive or undergoes a different sort of chemical change. Thus, dry, gaseous, or liquefied hydrogen chloride hardly interacts at all with zinc. Pure, concentrated sulphuric acid, on the other hand, although almost unaffected by zinc in the cold, is violently decomposed when heated. The action, however, is not a simple displacement of the hydrogen. The oxygen is removed from a part of the acid, and water and hydrogen sulphide are formed:

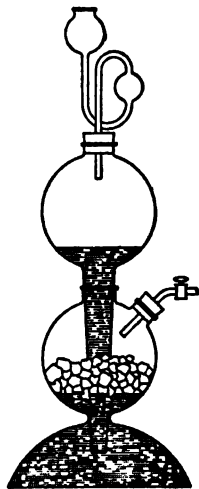


FIG. 43.

**Preparation of Hydrogen by Electrolysis.** — When we desire to liberate hydrogen by the direct application of energy (p. 28), we find that electrical energy serves the purpose best.

The common compounds of hydrogen, like hydrogen chloride and water, are not easily decomposed by heat, and in most cases, at best, a mixture of gases would be obtained. The difficulty in separating the resulting gases makes the use of this form of energy unsuitable. On account of its ability, not only to liberate the constituents from combination, but also to deliver the positive and the negative parts of the compound in *separate places*, electricity alone is available.

If we dissolve *any acid* in water, and immerse the wires from a battery in the solution, bubbles of hydrogen begin to appear on the *negative wire* (the cathode) and rise to the surface. All the other constituents, whatever they may be, form the negative radical (see above) and are attracted to the positive wire (the anode) and some of them are set free at its surface. An apparatus devised by Hofmann (Fig. 44) enables us to secure the hydrogen, which ascends on the left and accumulates at the top of the tube, displacing the solution. The other products, if gaseous, occupy a separate tube on the right side. The solution displaced by the gases is forced down and mounts into the bulb behind. The current of electricity flows from one wire to the other through the liquid in the cross-tube. In a typical case, the production of hydrogen ceases when the acid is all decomposed. The water alone is an almost complete nonconductor, so that the flow of the electricity practically ceases at the same time. If the operation does not come to rest in this way, its continuance is due to the regeneration of conducting substances by the interaction (with the water) of the materials of the radical liberated at the positive electrode.

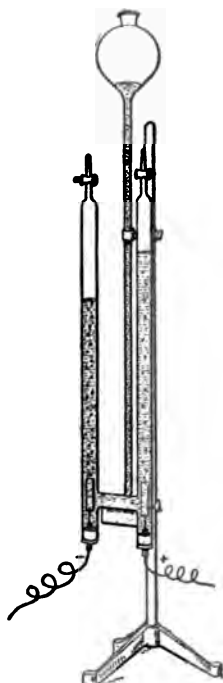
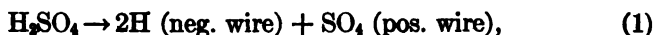


FIG. 44.

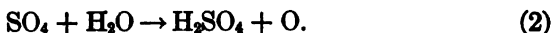
When hydrochloric acid is used, we have a close approximation to the typical case. The equation is:



and the chlorine, a soluble gas, remains dissolved in the water near one pole. When sulphuric acid is employed, the equation is:



and the  $\text{SO}_4$  interacts with the water (see Discharging potentials), thus:



Hence oxygen comes off, and the substance regenerated is here sulphuric acid itself. The final results are, therefore, the liberation of hydrogen and of oxygen and the localization of the regenerated acid round the positive electrode.

Decomposition of a compound by the use of electrical energy is called **electrolysis** (Gk. *ἤλεκτρον*, amber; *λύειν*, to loosen).

It is worth noting that the acids and water, taken separately, are all nonconductors. The fact that the *mixture* does conduct, concomitantly with the decomposition of the acid, is therefore highly suggestive. Solution in such cases must be something more than a mere physical change of state of aggregation (see Ionization).

It is commonly asserted that water is decomposed by a current of electricity. This is true in the sense in which we might say that a man can carry off a hill. He may eventually remove it, if you give him time. The action of electricity upon the purest water is exceedingly slow, on account of the very minute conductivity for electricity which it possesses. Common distilled water owes its appreciable capacity for conducting chiefly to traces of an acid, namely, carbonic acid, which it contains. Even when the water is saturated with carbonic acid, however, dilute sulphuric acid has a conductivity of the order of a thousand times greater. For our present purpose, therefore, water is declared to be a nonconductor. Yet, as we shall see, the conductivity of pure water, small as it is, has to be taken into consideration in certain cases (see Hydrolysis and Electromotive chemistry).

When dilute sulphuric acid is employed, the sulphuric acid is regenerated by interaction with the water, so that, in the end, only the water is decomposed. But the illustration is needlessly complicated by the chemical interaction of the  $\text{SO}_4$  with the water. The source of the hydrogen and the oxygen liberated is also rendered obscure by the fact that the sulphuric acid itself contains both of these elements. When an aqueous solution of sodium fluoride  $\text{NaF}$  is electrolyzed, the dissolved substance contains neither hydrogen nor oxygen. Neither the sodium nor the fluorine themselves can be liberated, however, because the hydrogen and oxygen of the water are more easily discharged and set free. In this instance, the salt renders the liquid a good conductor, which water alone is not, yet, in so far as decomposition of any substance is concerned, only the water is decomposed. This is a straight case of decomposing water by electrical energy.

**The Other Ways of Preparing Hydrogen.** — For special purposes, hydrogen may be made by boiling an aqueous solution of sodium hydroxide with aluminium turnings, when sodium aluminate is formed:  $\text{Al} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{NaAlO}_2 + 3\text{H}$ ; also by heating



powdered zinc and dry sodium hydroxide, the product being sodium zincate:  $\text{Zn} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{NaHZnO}_2 + 2\text{H}$ .

**Sources of the Hydrogen of Commerce.** — Zinc is too expensive a substance to use in the preparation of hydrogen in large quantities for commercial purposes. We realize this when we note that 33 parts of zinc will liberate only one part of hydrogen, so that with 1 lb. of zinc we obtain only one half-ounce of the gas. Different sources are used in different localities and countries.

The largest supply is probably obtained as a byproduct in the electrolysis of an aqueous solution of common salt  $\text{NaCl}$ , in connection with the manufacture of caustic soda (sodium hydroxide, *q.v.*). The hydrogen is collected and compressed in steel cylinders.

In some circumstances, the method of passing steam over heated iron is used (p. 116).

Another plan is to liquefy water-gas (*q.v.*), a mixture of hydrogen and carbon monoxide. The hydrogen evaporates much the more readily of the two, and can thus be separated. This, and still other processes involve substances and reactions which we have not yet encountered and will be mentioned at the appropriate points.

**Preparation of Simple Substances.** — There are two general sources from which we obtain simple substances. If the element occurs uncombined in nature, as sulphur and gold do, it is only necessary to free it from foreign materials (impurities) with which it is mixed. If no such supply exists, or if the purification is difficult, then some compound, natural or artificial, is decomposed.

The liberation of an element from combination is likewise effected in two ways: (1) The compound may be forced apart by the application of energy, usually in the form of heat or electrical energy. Thus, heat was employed to liberate oxygen (pp. 17, 82, 83). Electrical energy, however, was used in one way of obtaining hydrogen (p. 120), since readily obtainable compounds which, when heated, give hydrogen as the only gaseous product, are unknown. Electrical energy may be used also to liberate any metal. (2) The other general method of setting an element free is to offer to the other constituents of the compound some substance with which they will unite. This plan is used in liberating hydrogen from acids and from water (pp. 114–118).

In selecting our source, we are naturally influenced by the cost of the material, as well as by the ease of the process. Thus, gold oxide yields oxygen by the application of very little heat, but it is

extremely expensive. Quicklime is very cheap, but does not give up its oxygen even at the temperature of the electric arc. As a source of hydrogen, any acid may be used, theoretically, but the cheapest and commonest acids (hydrochloric acid and sulphuric acid) are actually employed.

**Purification of Gases.**—Hydrogen made in any of the above ways is impure (p. 6). As made by all the laboratory methods mentioned, a good deal of water vapor is mixed with it. Other impurities, like hydrogen sulphide and arsine, come from the action of the acid on foreign materials in the zinc (p. 119). Some of the acid, if it is volatile, will also be taken over with the gas. When the object for which the gas is being made demands it, we must know what the impurities to be expected are, and take proper means of removing them.

Gases are freed from aqueous vapor by means of calcium chloride or concentrated sulphuric acid, which greedily absorb moisture. The former is used in granulated form in straight or bent tubes (Fig. 45). The latter is applied by saturating pieces of pumice-stone with the acid and filling similar tubes with the fragments. Or the acid may be placed in a gas washing bottle (Fig. 46). For extremely complete drying, a tube may be filled with phosphoric anhydride sifted upon glass beads or glass wool. Forethought must be used to avoid a drying agent which will interact with gas. The longer the gas remains in contact with the drying agent, the more perfect, up to a certain limit, is the purification effected. In all cases, the stream of gas must pass slowly.

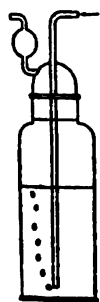


FIG. 46.

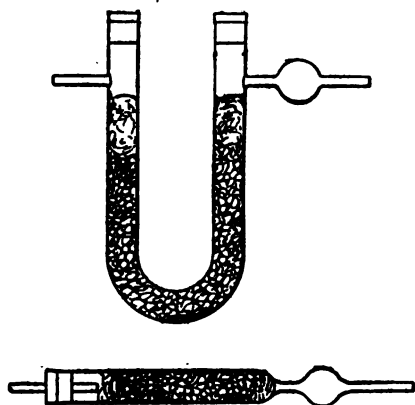


FIG. 45.

Particles of liquid or solid matter are always carried along by freshly made gases. These will pass with the gas through sulphuric acid without being affected. A plug of cotton or of glass wool in some part of the tubing is required to arrest them.

**Physical Properties of Hydrogen.**—Some of these may be given in tabular form:

Colorless	Crit. temp., $-234^{\circ}$
Tasteless	Sp. ht. (gas, const. press.), 3.4
Odorless	Boiling-point, $-252.5^{\circ}$
Density (air = 1), 0.0695	Melting-point (58 mm.), $-260^{\circ}$
Wt. of 1 l., 0.08987 g.	Sol'ty in Aq, 1.9 vols. in 100 ( $14^{\circ}$ )

Air is 14.5 times heavier, hence the gas may be poured upwards (Fig. 47) and is used for filling balloons.

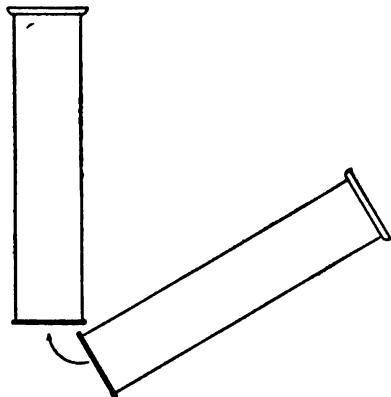


FIG. 47.

A liter flask filled with air requires about 1.2 g. to be added to the tare to restore the balance when the air is replaced by hydrogen. Its specific heat is about seventeen times that of oxygen (0.2). Its thermal conductivity is greater than that of any other elementary gas. Hence a wire, raised to incandescence in air by means of an electric current, cannot be kept at a red heat, even, by the same current in hydrogen. This is due to the fact that much of the heat is used, not merely to increase the velocity of the molecules, each of which contains

two atoms of hydrogen, but also to decompose them into atoms (see Chap. XII).

Hydrogen was first liquefied in visible amounts by Dewar (1898). The liquid is colorless and, when allowed to evaporate rapidly under reduced pressure, freezes to a colorless solid. All other gases, except helium, solidify easily when led into a vessel surrounded by liquid hydrogen.

Hydrogen is absorbed, for the most part in a purely mechanical way, by many metals. Heated iron will take up 19 times its volume of hydrogen. Under similar conditions gold takes up 46 volumes, platinum in fine powder 50 volumes, palladium 502 volumes, and silver none. The maximum absorbed by palladium under favorable conditions is 873 volumes. It is still a question whether, in the case of palladium, a part of the gas is not in combination.

**Diffusion.**— If a volume of gas is enclosed at one end of a cylinder, the rest of which is entirely empty, and is suddenly released from this confinement, it spreads with extreme speed so as to occupy the whole of the cylinder to an equal degree. This spreading is not an effect of gravitation, since it takes place upwards or downwards with equal celerity. The same phenomenon is observed when, in everyday life, a bottle of scent is opened. The vapor, on escaping, begins to penetrate in all directions through the room, showing its presence by its odor. The motion, as this instance shows, takes place through a space occupied by another gas more slowly than, but just as surely as, when the space is empty. The material of gases has in fact an independent power of locomotion. The resulting phenomenon we call **diffusion**. It is constant in rate for each gas under like conditions, and hydrogen has the greatest speed of diffusion of all the gases.

The interdiffusion of gases and the absence of gravity effect may be shown simultaneously. A jar of air is inverted and placed mouth to mouth with a jar filled with carbon dioxide (Fig. 48). After a few minutes, and in spite of the fact that carbon dioxide, measured in bulk, is one-half heavier than air, limewater will show the presence of carbon dioxide in the upper jar. The phenomena of diffusion must

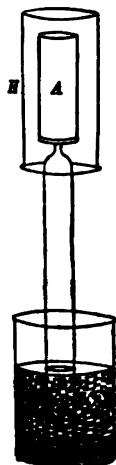


FIG. 49.

not be confused with cases like the pouring of hydrogen upward to displace air in an inverted jar. In this case the gas flows *en masse*, and the gravity effect is the very one on which we depend for the success of the experiment. It is when hydrogen scatters itself in a somewhat slower way, and downward and sideways as well as upward, that we have diffusion. The word indicates the *scattering* rather than the *flowing* nature of the phenomenon.

The different rates of diffusion of different gases are easily shown by comparing their several speeds with that of air, when both pass through a wall of unglazed, porous porcelain.

The cylinder of porous porcelain A (Fig. 49) contains air and is connected with a wide tube which dips beneath the surface of the water. When a cylinder H containing hydrogen is brought over it, rapid escape of gas takes place through the water, showing that a rise in pressure has taken place inside the porous vessel. Before the



FIG. 48.

cylinder of hydrogen approached it, the air was moving both outwards and inwards through the porcelain, but, being the same

air, the speed of motion was equal in both directions, and therefore the pressure inside was not affected. It is important to note that there was at no time rest, there was simply equal motion in both directions. When the hydrogen atmosphere surrounded the cylinder, the hydrogen gas moved more rapidly into the cylinder than the air inside could move out, and hence an excess of pressure quickly arose in the interior.

Exact measurement shows that the lighter a gas is in bulk, the faster its parts move by diffusion in any direction. The rate is inversely proportional to the square root of the density of the gas. Thus, for hydrogen and air it is in the ratio  $\sqrt{1.293} : \sqrt{0.08987}$ , or 3.8 : 1.

**Chemical Properties of Hydrogen.**—Hydrogen, delivered from a jet, burns in air or pure oxygen. A cold vessel, held over the almost invisible blue flame (Fig. 50), condenses to droplets of water

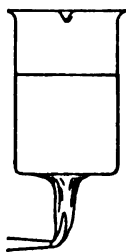


FIG. 50.

the steam that is produced. When hydrogen and oxygen are mingled in a suitable burner (Fig. 51), and the flame is allowed to play on a piece of quicklime, the latter becomes white-hot at the spot where the flame meets it. This result is called a **calcium light** or **lime light**. Platinum melts in this flame easily. In a closed space it produces a temperature of over 2500°.

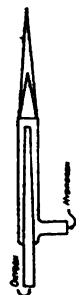


FIG. 51.

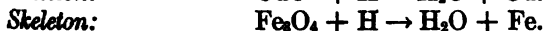
When oxygen and hydrogen are mixed in a glass vessel, the chemical action is very slow at ordinary temperatures, *no perceptible amount of union occurring in a period of five years*. If the mixture is sealed up and kept at 300°, after several days a small part is found to have combined to form water. At 518°, hours are required before the union is complete. At 600° the interaction is rapid, but not explosive. At 700° the combination is almost instantaneous. Hence contact with a body at a bright-red heat (p. 94) is required actually to explode the mixture.

These facts illustrate the effect of temperature on the speed of chemical changes (p. 93). A rough calculation shows that, since interactions lower their speed to half its value for every depression of 10° in temperature, at ordinary temperatures this union can hardly make easily perceptible progress in less than a thousand million years. This effect of temperature, therefore, accounts for the apparent absence of action in the cold gases.

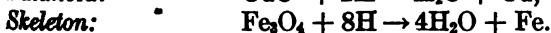
Finely divided platinum,\* when held in the cold mixture, hastens the otherwise vanishingly slow union in the part of the gases in contact with it. The heat of their union raises the temperature of the platinum to a white heat and this causes explosion of the whole mass of gas. The platinum is simply a contact agent (p. 97) and remains itself unaffected. The same explanation applies to self-lighting gas jets and to pocket cigar lighters.

Hydrogen unites directly with a minority only of the simple substances. It combines rapidly with oxygen, chlorine, fluorine, and lithium, and more slowly with a few others.

Hydrogen also unites with oxygen and chlorine, even when these elements are already combined with certain of the metals. Thus, when one of the oxides of copper or of iron is heated in a tube through which hydrogen flows, the latter combines with the oxygen to form water, and the metal is liberated:



We observe that, for each atomic weight of oxygen, 2H will be required, and amend the equations thus:



Then we take the amount of iron produced equal to that taken:



These interactions are classed, by mechanism, as displacements (p. 21). In describing them the chemist would also say that the hydrogen has been *oxidized* and that the oxide of the metal has been *reduced* (p. 91).

**An Inapt Use of the Word "Affinity" in Explanation of Chemical Actions.** — Speaking without reflection, one might be tempted to "explain" actions like the reduction of magnetic oxide of iron, just mentioned, by saying that the hydrogen has a greater tendency to unite with oxygen, or has a *greater affinity* for it, than has iron, and therefore removes the oxygen from combination with the latter. Plausible as this statement seems, it would be in many

\* The most convenient form is obtained by dipping asbestos in a solution of chloroplatinic acid, and heating it in the blast-lamp. The fibers are covered with a thin film of the metal:  $\text{H}_2\text{PtCl}_6 \rightarrow \text{Pt} + 4\text{Cl} + 2\text{HCl}.$

cases, as here, quite incorrect. Under the modes of preparing hydrogen, we spoke of the action of steam upon iron (p. 116), and gave the equation:  $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{H}$ . To use consistently this handy method of explaining chemical change by the help of the word "affinity," we should have to say here that the hydrogen has a *less affinity* for the oxygen than has iron; and therefore hydrogen is set free and oxide of iron is formed. It will be seen that this statement is in direct contradiction to the one made above. Both cannot be true. The fact is that both are based upon an assumption which is incorrect — the assumption, namely, that the displacement of one element by another is always an evidence of the greater affinity of the latter. The correct explanation of seemingly contradictory actions like these will be given later (see Hydrogen chloride)

The action of catalytic agents is itself a refutation of this blundering assumption. Putting a little platinum in a mixture of oxygen and hydrogen cannot add to the energy contained in these substances, and cannot therefore increase their intrinsic tendencies to unite. Yet in its presence an almost nonexistent action becomes suddenly explosively violent. There are other factors, often far more potent than affinity, which determine the direction and speed of many chemical changes (see Chemical equilibrium).

In this connection, it is worth noting that, while increasing the speed of a train or a ship requires a great addition to the energy expended, and is very costly, in increasing the speed of a chemical change requires the expenditure of no energy whatever. The employment of a couple (p. 119) or a catalytic agent adds nothing to the energy the separate bodies possessed before they were mixed. And the catalytic agent is recovered *unchanged* and as efficient as ever at the end. Theoretically, therefore, these agencies cost nothing. The increased speed in the formation of the products is obtained gratis. The contact method of making sulphuric acid (*q.v.*) illustrates the way in which commerce has taken advantage of this fact

**The Speed of Chemical Actions: a Means of Measuring Activity.** — The speed of a chemical action is measured by the number of atomic or formula weights of the substance undergoing change in a given time. Now, one means of measuring the relative chemical activities of several substances, is to observe the speed with which they undergo the same chemical change (p. 37). Thus we may compare the activities of the various metals by allowing them separately to interact with hydrochloric acid and collecting and measuring the hydrogen liberated per minute by each. It will be seen, even in the roughest experiment, that magnesium is thus much more active than zinc. The comparison must be made with such precautions, however, as will make it certain that the condi-

ions under which the several metals act are all alike. Thus, in spite of the heat evolved by the action, means must be used, by suitable cooling, to keep the temperature at some fixed point during all the experiments, for all actions become more rapid when the temperature rises (p. 93). Again, pure materials must be used, as an impurity in one metal might act as a contact agent and modify the natural speed of the action (p. 119). Still again, the pieces of the various metals must be arranged so that equal surfaces are exposed to the acid in each case. Equal weights of zinc will finally give equal weights of hydrogen; but if one of them is in the form of a coil while the other is a cylinder, the former, although it will not last so long, will give more hydrogen per minute. Finally, the portions of hydrochloric acid must contain the same percentage of hydrogen chloride in each case, for the metal will secure the acid it needs with less delay in a more concentrated solution than in a less concentrated solution, and in the former case will therefore displace hydrogen more rapidly. When these and other precautions have been taken, a true comparison of the relative activities of the metals with respect to this particular action may be made. It is found that the order in which this comparison places the metals is much the same as that in which they are placed by a study of other similar actions. This is natural, since we are really comparing, in each case, the amount of free, internal energy in each metal. A single table suffices, therefore, for all purposes (see next section).

***The Order of Activity of the Metals.***—We employ metals so frequently in chemistry, that we must at once become familiar with the key to the main differences in their behavior. The order of their activity explains these differences, as well as many other facts. In the adjoining list, the most active metals are at the top. Hydrogen is not a metal, but is included because chemically it resembles the metals. All the metals above hydrogen displace this element from dilute acids (and from water), while those below it do not.

The first displaces the hydrogen from water violently, the second

#### ORDER OF ACTIVITY. METALS.

Potassium  
Sodium  
Calcium  
Magnesium  
Aluminium  
Manganese  
Zinc  
Chromium  
Iron  
Nickel  
Tin  
Lead  
**Hydrogen**  
Copper  
Bismuth  
Antimony  
Mercury  
Silver  
Platinum  
Gold



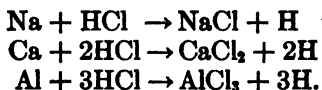
less vigorously. Magnesium barely acts on boiling water, but, like iron, acts on superheated steam. Zinc liberates hydrogen with reasonable vigor from dilute acids, lead rather feebly, and copper and those following not at all.

Other facts are explained by the table. Thus, when the metals are heated in pure oxygen, the last three do not combine. Those above silver do unite with oxygen — mercury rather slowly and the others more and more energetically as we ascend the list. Again, if we take the oxides of the metals, we find that those of the metals up to and including mercury lose all their oxygen when simply heated. If we heat the oxides, and also lead hydrogen over them, the oxygen is easily removed from all the oxides up to and including those of iron, leaving in each case the metal. Thus, in general, the more active metals form the most stable compounds.

The metals following hydrogen are the ones which are found in nature in large amounts in the free condition. Those preceding hydrogen, if liberated, since they all displace hydrogen from acids, would act slowly on natural waters containing carbonic acid, and so would pass into combination. Hence those preceding hydrogen are found free only in exceptional cases, such, for example, as the metallic iron of which meteorites often consist.

#### VALENCE

**Equivalence and Valence.** — If the equations showing displacement of hydrogen by a metal be now reexamined, a peculiarity will be noticed which we have thus far omitted to note. When sodium (p. 115) and calcium (p. 116) act upon water, one atomic weight (or atom) of sodium displaces one atomic weight of hydrogen, but one atomic weight of calcium displaces twice as much hydrogen. Again, one atom of zinc (p. 118) displaces two atoms of hydrogen, but one atom of aluminium displaces three. Assuming, for simplicity, that we allow three of these metals all to act upon dilute hydrochloric acid, the equations are:



Interpreting this, we perceive that the atom of aluminium, for example, displaces 3H, *because it is able to combine with 3Cl*, and so incidentally liberates the hydrogen formerly united with 3Cl. The

atom of sodium, however, can unite with only 1Cl, and so releases only 1H. Now this is not a rule confined to these reactions, but represents a general chemical property of the atomic weight of each element, and a property which we shall find most useful.

The atom of aluminium releases 3H because it can take the place of three atoms of hydrogen in chemical combination (and hold 3Cl). The atomic weight of aluminium is said to be *equivalent* to (equal in chemical value to) three atomic weights of hydrogen. Since it combines with 3 atomic weights of chlorine, it is also considered to be equivalent to three atomic weights of this element.

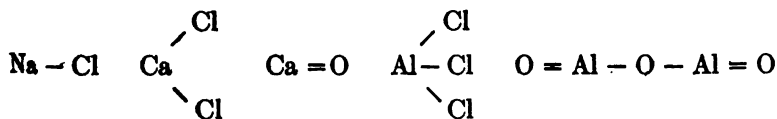
The *chemical property* referred to is called **valence**. The valence of an atomic weight of hydrogen or of chlorine is the unit. An atomic weight of sodium is said to be **univalent**, one of calcium **bivalent**, one of aluminium **trivalent**. The formula  $H_2O$  shows the atomic weight of oxygen to be bivalent, because it unites with two atomic weights of hydrogen. Apparently, the atomic weight (or atom) of each element has a fixed capacity for combining with not more than a certain number of atomic weights (or atoms) of some other element.

**Marking the Valence.** — Until we have become familiar with the valence of each element, it is advisable to mark the valences in a special way:  $Na^I$ ,  $Ca^{II}$ ,  $Al^{III}$ ,  $O^{II}$ ,  $Zn^{II}$ ,  $Cl^I$ .

As we should expect, a bivalent atom can combine with two univalent atoms, or with one bivalent atom, and so forth. Thus we have the compounds of oxygen:  $Na_2^I O^{II}$ ,  $Ca^{II} O^{II}$ ,  $Al_2^{III} O_3^{II}$ ,  $Zn^{II} O^{II}$ ,  $Cl_2^I O^{II}$ .

The rule is that the quantities of two elements which combine must have equal total combining capacities — i.e., identical total valence. Thus,  $Ca^{II}$  has the valence two, and so does  $O^{II}$ . Again,  $Al_2^{III}$  has a total valence of  $2 \times 3 (= 6)$  and so has  $O_3^{II}$  ( $3 \times 2 = 6$ ).

Frequently the valence is marked by means of lines, the number of lines pointing towards a symbol indicating the valence of the atom it represents:

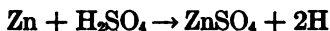


**Definition.** — The valence of an element is a number representing the capacity of its atomic weight to combine with, or displace,

atomic weights of other elements, the unit of such capacity being that of one atomic weight of hydrogen or chlorine.

Stated otherwise, the valence of the atomic weight (or atom) of an element is the number of atomic weights (or atoms) of hydrogen, or of some other univalent element, which the atomic weight (or atom) of the given element combines with or displaces.

- **Valence of Radicals.** — What we have said applies to compounds of not more than two elements — so-called **binary compounds**. We cannot with certainty tell the valences in a compound of three or more elements, like  $\text{H}_2\text{SO}_4$ . But we have seen that the acids behave as if composed of two radicals (p. 117):  $\text{H}(\text{Cl})$ ,  $\text{H}_2(\text{SO}_4)$ , that is, of two groups which move as wholes in chemical reactions. Thus, in the interaction of zinc with dilute sulphuric acid:



the group  $\text{SO}_4$  passes as a whole from combination with  $2\text{H}$  into combination with  $\text{Zn}$ . Hence we can assign a valence to a compound radical *as a whole*. Thus,  $(\text{SO}_4)^{\text{II}}$  is evidently bivalent, as a whole, because it is united with  $2\text{H}^{\text{I}}$ .  $\text{Na}(\text{OH})$  and  $\text{Ca}(\text{OH})_2$  show the radical **hydroxyl**  $(\text{OH})^{\text{I}}$  to be univalent.

It is to preserve the identity of the radicals, and to make them easily recognizable, that we write them in brackets and place the coefficient outside, as  $\text{Ca}(\text{OH})_2$  and  $\text{Al}_2(\text{SO}_4)_3$ , instead of using the forms  $\text{CaO}_2\text{H}_2$ ,  $\text{Al}_2\text{S}_3\text{O}_{12}$ , and so forth. The bracketed forms show more clearly which radicals are present. Since substances like these commonly interact by double decomposition (p. 20) or displacement (p. 18), as if the radicals were single elements, this mode of writing the formulæ enables us to use the valence values, and so readily to write equations for such actions. This artifice, justified as it is by the mode of interaction, reduces many substances containing three or more elements to binary compounds. In writing formulæ of inorganic compounds, we usually place the positive radical (p. 117) in front and the negative radical after it.

**Use in Making Formulæ and Equations.** — The chief use of the conception of valence is the very practical one of enabling us to write formulæ. In making equations we constantly need to know whether the chloride of an element, say magnesium, is  $\text{MgCl}$ , or  $\text{MgCl}_2$ , or  $\text{MgCl}_3$ , or  $\text{MgCl}_4$ , etc., and whether its sulphate is  $\text{MgSO}_4$ , or  $\text{Mg}_2\text{SO}_4$ , or some other combination of the symbols. To answer

questions like this it is not necessary to know the formula of every compound of each element: the apparent disorder of these numbers can be reduced to rule, and the reader should endeavor thoroughly to master the rule before going farther.

Thus, suppose that we require the formula of aluminium hydroxide. Up to this point, we should have been compelled to look for it in a book. And if, later, we needed the formula of aluminium sulphate, we should have had to look that up, separately, also. But now, all we need is to know the valence of aluminium  $\text{Al}^{\text{III}}$ , of the hydroxyl radical  $(\text{OH})^{\text{I}}$ , and of the sulphate radical  $(\text{SO}_4)^{\text{II}}$ . Making the total valences in each half of each compound alike, we write the formulæ  $\text{Al}^{\text{III}}(\text{OH})_3^{\text{I}}$ ,  $\text{Al}_2^{\text{III}}(\text{SO}_4)_3^{\text{II}}$ .

The reader must make a special effort to note the valences of each element and radical, and always to use them in making formulæ. If a formula is written from memory, the valences must be checked, to make sure that the formula is correct.

**How to Learn the Valence of an Element.** — To find out the valence of an element, we must obtain the formula of one simple compound of the element, containing another element of known valence. Thus, what is the valence of carbon? Its oxide is  $\text{CO}_2$ . The total valence of oxygen here is  $2 \times 2 = 4$ . Carbon  $\text{C}^{\text{IV}}$  is therefore **quadrivalent**. Hence its chloride must be  $\text{C}^{\text{IV}}\text{Cl}_4^{\text{I}}$  (carbon tetrachloride), and its compound with hydrogen  $\text{C}^{\text{IV}}\text{H}_4^{\text{I}}$  (methane, composing a large part of natural gas). When carbon combines with a trivalent element, equi-valent amounts of each element must be used, as in  $\text{Al}_4^{\text{III}}\text{C}_3^{\text{IV}}$  (aluminium carbide), where  $\text{Al}_4^{\text{III}}$  and  $\text{C}_3^{\text{IV}}$  contain  $3 \times 4$ , or 12 units of valence each.

Again, when we know the formula of sodium iodide to be  $\text{Na}^{\text{I}}\text{I}$ , or that of hydrogen iodide to be  $\text{H}^{\text{I}}\text{I}$ , we infer that iodine is univalent. The formula of silica (sand)  $\text{SiO}_2^{\text{II}}$  shows silicon to be quadrivalent, and indicates that the chloride must be  $\text{SiCl}_4$ . Similarly the formula of calcium carbonate  $\text{Ca}^{\text{II}}\text{CO}_3$  shows that the radical  $\text{CO}_3$ , which is common to all carbonates, must be bivalent.

The chemist does not memorize the valences themselves; he recovers the valence of an element or radical, when needed, by recalling the formula of a substance containing this element or radical in combination with a more familiar element or radical, such as  $\text{Cl}^{\text{I}}$  or  $\text{H}^{\text{I}}$ .

**Elements with More than One Valence.** — The rule of valence is somewhat complicated by the fact that many elements show

more than one valence. In other words, the combining capacity of an atomic weight of such an element may have two (or even more) valences, according to the conditions under which the action takes place. This is as much as to say that an atomic weight of such an element may form stable compounds with two, or even more different numbers of equivalents of another element. This fact has already been mentioned, for it is implied in the law of multiple proportions (p. 58).

Thus, we have encountered two chlorides of iron, ferrous chloride  $\text{Fe}^{\text{II}}\text{Cl}_2$  and ferric chloride  $\text{Fe}^{\text{III}}\text{Cl}_3$ . We have, in fact, two complete series of compounds of iron, such as:

*Bivalent (Ferrous):*  $\text{FeCl}_2$ ,  $\text{FeO}$ ,  $\text{FeSO}_4$ .

*Trivalent (Ferric):*  $\text{FeCl}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$ .

When an element forms two such series of compounds, we always call particular attention to the fact.

As a rule, an element passes from one form of combination to another without change of valence. But compounds of elements like tin can also undergo changes in course of which the valence alters. Cases of this kind will be considered when they arise (see Preparation of chlorine).

**Exceptional Valences.**—Some elements show an exceptional valence in one compound. The valences shown in series of compounds are the important ones, and the exceptions need not particularly concern us. Thus, in addition to the oxides  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ , iron gives the magnetic oxide  $\text{Fe}_3\text{O}_4$ , where the valence of iron appears not to be a whole number, but  $\frac{8}{3}$  or  $2\frac{2}{3}$ . The valence is made regular by supposing the oxide to be a compound of the other two oxides, as if the formula were  $\text{FeO}, \text{Fe}_2\text{O}_3$ .

**Nomenclature.**—The names of compounds containing only two elements (the true binary compounds) end in *ide*. Such are the *oxides*, as ferric oxide  $\text{Fe}_2\text{O}_3$ ; the *carbides*, as aluminium carbide  $\text{Al}_4\text{C}_3$ ; the *chlorides*, as sodium chloride  $\text{NaCl}$ ; the *sulphides*, as ferrous sulphide  $\text{FeS}$ , etc. This applies also to compounds containing *positive* compound radicals, as ammonium chloride  $(\text{NH}_4)\text{Cl}$ .

When an element forms two (or more) compounds with another element, they are frequently distinguished thus: carbon *dioxide*  $\text{CO}_2$ , carbon *monoxide*  $\text{CO}$ ; phosphorus *pentoxide*  $\text{P}_2\text{O}_5$ , phosphorus *trioxide*  $\text{P}_2\text{O}_3$ .

To distinguish two compounds of the same elements, another plan is also used; ferrous chloride  $\text{FeCl}_2$ , ferric chloride  $\text{FeCl}_3$ ; mercurous oxide  $\text{Hg}_2\text{O}$ , mercuric oxide  $\text{HgO}$ . The suffix *ous* indicates that the metal is combined with the smaller proportion of the negative element, and *ic* that it is combined with the larger proportion.

The tendency — although not a universal rule — is to use the latter plan with compounds containing a metal and the former with compounds containing only non-metals.

***Valence and Equivalent Weights: A Different Viewpoint.***

— In the foregoing discussion of valence, we have more than once used the word “equivalent.” If the method by which the atomic weights were derived from equivalents (p. 63) be now reexamined, a different, and instructive view of the nature of valence will be obtained. It was found, for example, that 9.03 parts of aluminium (p. 63) combined with the equivalent weights of the other elements, and therefore with 35.46 parts of chlorine. If this weight of aluminium had been accepted as the final unit (the atomic weight), then it would have been represented by the symbol  $\text{Al}$ ; and, since  $\text{Cl}$  stands for 35.46 parts of chlorine, the formula of the chloride would have been  $\text{AlCl}$ . In point of fact, however, a number three times as large as the equivalent, namely 27.1, was chosen as the atomic weight of aluminium, and the symbol  $\text{Al}$  stands for this triple quantity. If the equivalent of chlorine had also been tripled in making its atomic weight, the amounts represented by the symbols would still have been chemically equivalent and the formula would still have been  $\text{AlCl}$ . But the equivalent of chlorine was left unaltered. Hence, to get the equivalent amounts (*i.e.*, the actual combining quantities) of the two elements, we must have  $3\text{Cl}$  with  $1\text{Al}$ . The formula is thus  $\text{AlCl}_3$ . Now, it is evident that this tripling of the equivalent of aluminium will affect the formulæ of *all* its compounds. Whenever it is combined with an element which, like chlorine, has identical equivalent and atomic weights, the formula of the compound will be of the form  $\text{AlX}_3$ . In accordance with this we have the bromide  $\text{AlBr}_3$ . In making the formulæ of compounds of aluminium, the chief thing to be kept in mind, therefore, is the fact that its atomic weight contains three equivalents and always combines with three equivalents of another element. This fact we state by saying that the **valence** of the atomic weight of aluminium is three, or simply that the **element aluminium is trivalent**.

Similarly, the equivalent of tin is 59.5 and its atomic weight is 119. This atomic weight therefore contains two equivalents of tin and combines with two equivalents of any other element. Hence, the formula of a compound of tin with an element of the chlorine class will be  $\text{SnX}_2$ . Thus tin is **bivalent**. In like manner the equivalent of sodium is 23, and this number was not altered in making the atomic weight. Hence, the symbol Na stands for one equivalent, and the formula of the compound with chlorine is NaCl. Elements whose atomic weights are identical with their equivalents are described as **univalent**.

Thus the **valence of an element** may be defined as the **number of equivalent weights contained in its atomic weight**. Arithmetically it is the integer by which the equivalent weight was multiplied in forming the atomic weight.

The above mode of handling valence is based upon the notion of *combination* in equivalent proportions. Another variety of chemical change, namely *displacement* (p. 18), is often of assistance in enabling us to determine the valence of an element. It will be noted that when Al acted upon hydrochloric acid (p. 118) and combined with 3Cl, it necessarily displaced the 3H with which the 3Cl was formerly united. It was *equivalent* to 3H for the purpose of holding 3Cl in combination. It is from this aspect of the relation that the word "valence" comes. Al is *equi-valent* to 3H, and, H having the unit valence, Al is trivalent. Similarly, since one atomic weight of zinc, represented by the symbol Zn, displaces 2H (p. 118) zinc must be bivalent. Combining this with the former conception, we reach a definition of the valence of an element: **The valence of an element is the number of equivalent weights which its atomic weight contains and is therefore the number of equivalent weights of another element or radical which its atomic weight is able to combine with or displace.**

It will be seen that the equivalent weight can always be found by a quantitative experiment. It is also evident that it is equal to the atomic weight divided by the valence. It is likewise clear that the equivalent weight of an element, multiplied by the valence of that element, is equal to the atomic weight. The conception of equivalent weight finds application in several connections in chemistry (see Normal Solutions and Faraday's Law).

As we have seen (p. 134), the regular valence of an element cannot be learned by examining the composition of a compound chosen at random. Thus FeS,  $\text{H}_2\text{S}$ ,  $\text{HgS}$ , and other compounds show sulphur to be bivalent. There is also a series in which sulphur is *sexivalent* in  $\text{SO}_2$ . But the compound  $\text{S}_2\text{O}_8$ , in which

sulphur appears to be trivalent, is an isolated case. Again,  $\text{FeO}$ ,  $\text{FeS}$ ,  $\text{FeCl}_2$ , show iron to be bivalent, and  $\text{FeCl}_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$ , etc., show it to be also trivalent. But  $\text{Fe}_3\text{O}_4$ , the magnetic oxide, is an exception. Valence has to do mainly with chemical *interactions*, in which the element either passes from one state of combination to another without change of valence, or goes over into a compound of another regular series with another regular valence. It is not a matter of statics. Hence, questions as to the magnitude of the valence in isolated compounds like  $\text{Fe}_3\text{O}_4$ ,  $\text{N}_2\text{O}$ , and so forth, are at present of minor importance.

A definition of valence differing from those given above is preferred by many chemists. The atomic weight of a univalent element can hold but one unit of another element in combination. Thus, the weight of chlorine represented by Cl can hold but one H or one Na in combination. An atomic weight of a bivalent element, although it combines with but one unit of another bivalent element, may hold as many as two units of a univalent element in combination. But it cannot hold more. A unit of a trivalent element, however, may hold as many as three units, provided the other element is univalent. In this point of view the **valence of an element is the maximum capacity of its atomic weight to hold atomic weights of other elements in combination.**

**Oddities Connected with Valence.** — When the conception of valence was first evolved, it was taken for granted, quite mistakenly, that each element had only one valence. Hence, when pairs of compounds like  $\text{CuCl}$  and  $\text{CuCl}_2$ , or  $\text{HgCl}$  and  $\text{HgCl}_2$ , or  $\text{FeCl}_2$  and  $\text{FeCl}_3$  were considered, and it was assumed that copper was *always* bivalent, mercury bivalent, and iron trivalent, the formulæ had to be distorted to fit this assumption. Hence the formula of cuprous chloride was written, and is still often written,  $\text{Cu}_2\text{Cl}_2$ . The formulæ of the two chlorides, written graphically (p. 131) then became:  $\text{Cl} - \text{Cu} - \text{Cu} - \text{Cl}$  and  $\text{Cl} - \text{Cu} - \text{Cl}$ . In both, each atom of copper was holding (on paper) two other atoms, and was therefore bivalent (on paper). Similarly doubling  $\text{HgCl}$  gave  $\text{Cl} - \text{Hg} - \text{Hg} - \text{Cl}$ ,

and doubling  $\text{FeCl}_2$  gave  $\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{Fe} \\ \diagup \\ \text{Cl} \end{array} - \begin{array}{c} \text{Cl} \\ \diagdown \\ \text{Fe} \\ \diagup \\ \text{Cl} \end{array}$ , where the mercury appeared to

be bivalent and the iron trivalent. Later, however, when elements like indium were found to have three valences, *e.g.*,  $\text{InCl}$ ,  $\text{InCl}_2$ , and  $\text{InCl}_3$ , and the compounds of manganese could not be classified unless five different valences were admitted, and many other elements turned out to be multi-valent, the idea of a fixed valence for each element was given up. It is entirely contrary to the scientific method to invent or to distort facts so as to procure support for a notion which is a mere assumption, and not founded upon experiment. Yet, the history of the science shows that such errors were frequently committed.

The fact is that a free element, like mercury, has no valence, for its atomic weight is not combined with even one equivalent of any other element. When combined, mercury shows two different valences, as in  $\text{Hg}_2\text{O}$  and  $\text{HgO}$ ,  $\text{HgCl}$  and  $\text{HgCl}_2$ ,  $\text{HgNO}_2$ , and  $\text{Hg}(\text{NO}_3)_2$ .

It is only in the chemistry of carbon that the prejudice in favor of a single valence still persists. All chemists admit that in carbon monoxide  $\text{CO}$  the



carbon is bivalent. But not all chemists admit that it is also bivalent in fulminic acid  $\text{H}-\text{O}-\text{N}=\text{C}$  and in the isonitriles  $\text{R}-\text{N}=\text{C}$ . For the unsaturated compounds, like ethylene  $\text{C}_2\text{H}_4$ , and acetylene  $\text{C}_2\text{H}_2$ , all chemists write the formulæ  $\text{H}_2=\text{C}=\text{C}=\text{H}_2$ , and  $\text{H}-\text{C}\equiv\text{C}-\text{H}$ , although there is at present no experimental evidence that the formulæ  $\text{H}_2=\text{C}-\text{C}=\text{H}_2$  and  $\text{H}-\text{C}-\text{C}-\text{H}$ , in which the carbon is trivalent and bivalent, respectively, do not represent the facts equally well, so far at least as valence is concerned. When triphenylmethyl  $(\text{C}_6\text{H}_5)_3\text{C}$  was discovered by Gomberg, it seemed as clear that in this substance one atom of carbon was trivalent, as that the copper in  $\text{CuI}$  is univalent; but violent efforts were made to avoid this obvious conclusion. For example, it was suggested that three of the valences held one  $\text{C}_6\text{H}_5$  group each, and that the fourth valence was divided amongst the three groups (partial valence). But valence goes by multiples of one equivalent, and this idea involved *splitting* one valence into thirds of an equivalent. The *affinity* of the carbon atoms is doubtless all divided amongst the three groups, so long as no fourth group is present to share it, for affinity is not divided into any definite number of units. This is a case of unconsciously confusing valence and affinity. If we venture thus to ignore the facts, then logically we must assume that in  $\text{FeCl}_3$  the iron is trivalent, and the third valence, in the absence of a third atom of chlorine, is being employed on the other two. Clearly every element, including carbon, is entitled to use all the different valences which are arithmetically possible, up to the maximum which it ever exhibits. The valence of iron (or carbon) in a given compound is not the maximum valence that it shows in some other compound, but the valence it is actually *using* in the compound in question, just as the money a man has in his pocket is the amount actually there, and not some larger amount we think he ought to have.

Finally, it may be noted that univalent, bivalent, and trivalent are terms of Latin derivation. But tetravalent is a hybrid, a mixture of Greek and Latin. One should use either the Latin numerals or the Greek numerals, exclusively. In this book the Latin ones are employed and the remaining valences are quadrivalent, quinquivalent, sexivalent, septivalent, and octovalent.

**Inept Definitions of Valence.** — No conception in chemistry is more frequently defined loosely or even inaccurately than is valence. Thus, one type of definition runs somewhat as follows: "The valence of an element is the number of atoms it can combine with or displace." Before criticising a general statement, it is well to substitute concrete things for the general terms. "The valence of oxygen is the number of atoms oxygen can combine with or displace." The number of atoms, say of hydrogen, with which oxygen can combine depends entirely on *how much* oxygen is available. A ton of oxygen will combine with many more than an ounce, and an ounce with many more than an atom. But this type of definition omits to specify the amount of oxygen, namely the atomic weight, or atom, to which the definition of valence alone applies. Oxygen, as a substance, is a general term — unlimited as to amount — so that according to this definition, the valence of every element must be infinity! The valence is not

a property of the element in general, but only of its atomic weight (or atom), and so the atomic weight must be mentioned. "The valence of an atom of an element is the (maximum) number of atoms it can combine with or displace." Or "the valence of an element is the (maximum) number of atoms its atom can combine with, etc."

Almost every published discussion of valence employs the word **power**. Thus: "Valence is the power of the atom of an element to hold atoms of other elements in combination." Now power is defined in physics as the rate at which a machine does work. Valence — say that in a pound of salt — does no work whatever. Hence, when the word power is used, the valence of every element becomes, *ipso facto*, zero! This definition goes to the opposite extreme of error from the last. The word suggests, and is perhaps intended to suggest, that valence is a measure of the force with which the atoms are held together in a compound. But valence has nothing to do with the force — which is a question of affinity — but solely with the quantity of matter held in combination. Thus, gold is trivalent ( $\text{AuCl}_3$ ), but the chloride can be decomposed by gentle heating, while sodium is univalent, yet, its chloride  $\text{NaCl}$  can be vaporized at a high temperature without decomposition. So an atom of gold holds three times as much chlorine in combination as does an atom of sodium (and is trivalent), although it holds it very feebly, or, as one might say, with little force or "power." Valence is the *number* of equivalents combined with the given atomic weight: it is simply a question of **capacity** (see definition, p. 137). A tank might have a capacity of a hundred million gallons of water, yet, if the tank were close to the sea level, the available *power* would be almost zero. Capacity and force and power are entirely different conceptions. The atom of some element might be able to hold eight atoms of hydrogen in combination — that would be its capacity or valence — yet, it might hold them so feebly (with so little force or "power") that the compound would give off hydrogen at room temperature, and would have to be kept in a refrigerator. Correct use of technical terms is indispensable in chemistry, and capacity, not power, is the term applicable to valence.

**Exercises.** — 1. Make equations for reactions in which hydrogen is liberated by the action of: (a) hydrochloric acid and magnesium, giving  $\text{MgCl}_2$ , (b) steam and zinc, giving  $\text{ZnO}$ .

2. Make an equation for the action of heat on manganese dioxide  $\text{MnO}_2$ , giving oxygen and  $\text{Mn}_2\text{O}_3$ .

3. What must be the relative rates of diffusion of hydrogen and of carbon dioxide?

4. Make equations to represent, (a) the reduction of lead dioxide  $\text{PbO}_2$  by hydrogen; (b) the actions of aluminium upon cold water and upon steam at a red heat.

5. Which are the components (p. 7) of dilute sulphuric acid and which are the constituents of sulphuric acid?

6. What are the valences of the negative radicals of phosphoric

acid  $\text{H}_3\text{PO}_4$ , and of acetic acid (p. 117)? What must be the formulæ of calcium phosphate, cupric acetate (p. 118), aluminium phosphate, ferrous carbonate, ferrous sulphate, cupric chloride?

7. What is the valence of phosphorus in phosphoric anhydride (p. 90)? What must be the formulæ of, (a) the corresponding chloride and the sulphide of phosphorus, and (b) of aluminium oxide?

8. What are the valences of the elements in the following:  $\text{LiH}$ ,  $\text{NH}_3$ ,  $\text{SeH}_2$ ,  $\text{BN}$ ?

9. What are the valences of the metals and radicals in the following:  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Ce}(\text{SO}_4)_2$ ,  $\text{KCl}$ ,  $\text{KMnO}_4$  (potassium permanganate)? Name all the substances in 8 and 9.

10. Write the formulæ of ferrous and ferric oxides, of ferrous and ferric nitrates, of stannous and stannic sulphides.

11. One gram of a quadrivalent element unites with 0.27 g. of oxygen. What is the atomic weight of the element?

## CHAPTER VIII

### WATER

THE great quantity of water which occurs in nature makes it one of the most familiar chemical substances. The ocean covers about three-fourths of the surface of the earth, and in most habitable regions lakes and streams abound. The "dry" land is, fortunately, far from being really dry. Water is found also in the bodies of both animals and plants in large quantities, and is indeed essential to the working of living organisms.

*Natural Waters.* — The water found in nature varies greatly in the amount of foreign material which it contains. Sea-water holds about 3.6 per cent of solid matter in solution, while rain-water is the purest natural water. Even rain-water contains foreign matter, however. When we heat it, bubbles of gas form on the sides of the vessel, showing that oxygen, nitrogen, and carbon dioxide from the air have been dissolved by the water as it fell. On evaporating a considerable mass of such water, we find that, aside from dust, crystals of chemical substances, such as ammonium nitrate, may be recognized in the residue. Of well and surface waters, some which contain calcium sulphate, calcium bicarbonate, and compounds of magnesium in solution are described as *hard*. Others contain compounds of iron, and still others are effervescent and give off carbon dioxide. These are called mineral waters. All of the dissolved substances are obtained by the water in its progress over or under the surface of the ground.

Water which is to be used for domestic purposes is examined, not only to ascertain the amount of the ingredients which produce hardness, but also with reference to the proportion of organic matter which it may hold in solution. This usually gains access to the water by admixture of sewage (p. 92). It is not the organic matter itself which is deleterious, but the bacteria of putrefaction and disease which are likely to accompany it. If the water contains clay in suspension, the bacteria are largely attached to the particles of clay, but organic matter and bacteria may be present in water which looks perfectly

clear. Inoculation of culture media with the water can alone show whether or not bacteria are present.

The foreign materials which water may contain are divisible into two kinds—**dissolved** matter and **suspended** matter. No natural water is entirely free from either of these varieties of impurity.

**Purification from Suspended Matter and Bacteria.**—The suspended impurities may be removed by filtration. On a large scale, beds of gravel are employed, but this treatment will not remove all bacteria. In many cases small amounts of alum, or alum and lime, or ferrous sulphate (copperas) and lime, are added. These produce slimy precipitates which assist in the elimination of fine, suspended inorganic and organic matter, including practically all bacteria. This is called the **coagulation treatment** (*q.v.*). The whole suspended matter is then allowed to settle, which it does very quickly, in large reservoirs. The remaining organisms may be destroyed by adding a little bleaching powder (*q.v.*), or chlorine-water, before the water is distributed. Ozone (*q.v.*) and ultra-violet light are used for the same purpose, the latter, for example, at Rouen. The ultra-violet light, which is a light of very short wave length, is produced by an electric arc passing through mercury vapor in a container of quartz (glass absorbs and destroys this light). The water must first be filtered so that the light may be able to penetrate it. A 3-ampere lamp on a 220-volt circuit will kill the colon bacilli, organisms associated with those which produce typhoid fever, in a layer of water 10 cm. thick in 1 second and in a layer 40 cm. thick in fifteen seconds. The flow of the water is regulated so as to permit sufficiently long exposure to the rays.



FIG. 52.

In the household, the **Pasteur filter** is the most compact and efficient appliance. The water enters at the top (Fig. 52) and is forced inwards by its own pressure through the pores of a cylinder of un glazed porcelain. The cylinder must be taken out, and its exterior cleaned daily with a brush, to remove the mud and organisms which collect on its outer surface. If this is not done, the organisms multiply and soon the filter pollutes the water instead of purifying it.

Most organisms can be killed by boiling unfiltered water for 10 or 15 minutes, although a second boiling is needed in some cases.

**Purification from Dissolved Matter.**—Filtration does not remove dissolved matter, and therefore does not soften hard water (*q.v.*).

Pure water for chemical purposes is prepared by distillation and, in fact, liquids other than water are usually purified by the same process (Fig. 20, p. 43). The steam is condensed by cold water circulating in the jacket, and contains at first only gases dissolved from the air. The dissolved solids remain in the flask. Distilled water quickly dissolves traces of glass or porcelain, so that the purest water is obtained by using quartz or platinum for the condenser tube and receiving vessel. Tin is the best of the less expensive materials.

That glass dissolves in water is easily shown by shaking some pulverized glass with distilled water for a few seconds and adding a drop of phenolphthalein solution (see Indicators). The alkaline reaction of the dissolved sodium silicate gives rise to a strong pink color [Lect. exp.].

**Physical Properties of Water.**—When we view a white object through a deep layer of water we find that the liquid has a blue or greenish-blue color. At a pressure of 760 mm., water exists as a liquid between 0° and 100°. Below 0° it becomes solid, above 100° a gas. Of all chemical substances it is the one which we use most, so that familiarity with its physical properties, discussed below, is indispensable to the chemist. It will serve also as a typical liquid, since it differs from others only in details.

The quantity of heat required to raise one gram of water one degree in temperature, at 15°, is called a **calorie**, and is the unit of heat. The specific heat of any substance being also the quantity of heat required to raise the temperature of one gram of the substance one degree, the specific heat of water is 1. The values for other substances are all smaller (*e.g.*, limestone 0.2). Thus the temperature of large masses of water, such as lakes and seas, changes more slowly, and within a smaller range, than that of the rocks and soil composing the land. The more constant temperature of the water tends to regulate that of the air, and hence the climate of islands is less variable from season to season than is that of a continent.

The weight of a cubic centimeter of water at 4° gives us our unit, the gram. A kilogram of water at 0° occupies 1.00013 liters, or 0.13 c.c. more than at 4° C. A kilogram of ice at 0° occupies 1.09083 liters, or 90.7 c.c. more than an equal weight of water at 0°. The volume of one kilogram of water at 100° is 1.0432 liters.

**Ice.** — The raising or lowering of the temperature of a gram of water through one degree corresponds to the addition or removal of one calorie of heat. The conversion, however, of a gram of water at  $0^{\circ}$  to a gram of ice at  $0^{\circ}$  requires the removal of 79 calories of heat. The mere melting of a gram of ice causes an absorption of heat to the same amount. This is called the **heat of fusion of ice**. At  $0^{\circ}$  a mixture of ice and water will remain in unchanged proportions indefinitely. Any cause which tends *permanently* to lower or raise the temperature by a fraction of a degree, however, will bring about the disappearance of the water or of the ice, respectively. This temperature ( $0^{\circ}$ ) is called the **melting-** or the **freezing-point** of water. Properties of this kind, marked by **transition points** from one state to another, are much used in chemistry for keeping other bodies or systems at a constant temperature during measurement or observation. A mixture of ice and water surrounding a body, when kept in constant agitation, will automatically maintain the body at a fixed temperature ( $0^{\circ}$ ) so long as both components hold out.

Water can easily be cooled below  $0^{\circ}$  (**supercooled**) without beginning to freeze, unless it is stirred or "inoculated" by the addition of a piece of ice. Hence, the freezing-point is not defined as the point at which ice begins to form, for that point varies, and is always below  $0^{\circ}$ , but as the temperature of a well-stirred *mixture* of ice and water.

**Steam.** — At atmospheric pressure, water passes into steam rapidly at  $100^{\circ}$ , but at lower temperatures, and even when frozen, it does the same thing more slowly. It changes into steam, however, only when the necessary supply of heat is forthcoming. One gram of water at  $100^{\circ}$ , for example, in turning into a gram of steam at  $100^{\circ}$ , takes up 540 calories. This is called its **heat of vaporization**. Steam, in fact, contains much more internal energy than an equal weight of water at the same temperature, just as water, in turn, contains more energy than ice.

Steam is a colorless, invisible gas. The visible cloud of fog, seen when steam escapes into cold air, is composed of minute drops of water, formed by condensation, and visible because they have *surfaces* which reflect light.

The temperature of  $100^{\circ}$  is, like the melting-point of ice, an important transition point. It is less exactly recoverable by simply keeping a vessel full of water in ebullition, however, because the natural, and often considerable, variations in the pressure of the

atmosphere affect it more markedly than they do the melting-point of ice. Near to  $100^{\circ}$ , the boiling-point rises or falls about  $0.037^{\circ}$  for 1 mm. change in pressure. On the top of Mont Blanc water boils at  $84^{\circ}$ . The melting-point of ice is lowered only  $0.0075^{\circ}$  by an increase in pressure from 760 mm. to 2 atmospheres (1520 mm.)

Most substances are known in three different states of aggregation, solid, liquid, and gaseous. There is no magic about the number, three, however. Thus, sulphur has a vapor state, two liquid states, and at least four different solid forms. There are even five different forms of ice, and most solids probably exist in several different states.

**Vapor Pressure and Aqueous Tension.** — The quantity of vapor given off by a substance is defined by the gaseous pressure it exercises. This is called the **vapor pressure** of the substance.

The most significant fact about vapor pressure is that, *when excess of the liquid is present*, the pressure of the vapor quickly reaches a definite maximum value for each temperature. In the absence of excess of the water, *less* than this maximum pressure may exist. *More* than the maximum pressure proper to a given temperature, if produced by compression, cannot be maintained, however, for a part of the vapor condenses to the liquid state. The magnitude of this maximum vapor pressure, at a given temperature, depends on the ability of the particular liquid to generate vapor. This maximum vapor pressure is held, therefore, to represent the **vapor tension of the liquid**, at the given temperature, and this is a specific property of the substance.

The vapor tension may be shown by allowing a few drops of water to ascend into the vacuum at the top of a barometric column (Fig. 53). The tube on the left shows the mercury when nothing presses on its surface. The tube on the right shows the result of admitting the water. The pressure of the atmosphere being the same for both, the smaller height of mercury which now suffices to counterbalance it shows that something, which can be nothing but the water vapor, is pressing on the surface of the mercury, and makes up the rest of the total stress needed. The difference in the height of the two columns gives the value of this pressure, which we call the **vapor pressure of the water**.

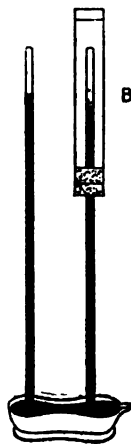


FIG. 53.



With excess of liquid water, the value is that of the vapor tension of the liquid, called, in the case of water, the **aqueous tension**.

The jacket surrounding the tube on the right enables us, by adding ice or warm water, to keep the water that is admitted to the vacuum, and the parts of the apparatus immediately in contact with it, at any temperature between  $0^{\circ}$  and  $100^{\circ}$ . When ice is used outside, and a piece of it is introduced into the vacuum, the vapor it gives off quickly reaches a pressure of 4.5 mm. The vapor pressure of the ice takes the place of 4.5 mm. of mercury in balancing the atmospheric pressure, and so the mercury column falls by this amount. Similarly, water at  $10^{\circ}$  causes a fall of 9.1 mm. and at  $20^{\circ}$  of 17.4 mm., so that these represent the mercury-height values of the aqueous tension at these temperatures. With ether, instead of water, at  $10^{\circ}$ , the fall is 28.7 mm. The *quantity* of water used makes no difference, so long as a *little more* is present than is required to fill the available space with vapor. Of course, if a large amount is admitted, its dead weight will take the place of an equal weight of mercury in balancing the pressure of the air. If there is a measurable column of water, its height must be divided by 13.6 (the density of mercury), and counted as if it were part of the mercury.

With water at higher temperatures the fall of the mercury column becomes much greater. At  $50^{\circ}$  it is 92 mm., at  $70^{\circ}$  it is 233.3 mm., at  $90^{\circ}$  it is 525.5 mm., and at  $100^{\circ}$  it is 760 mm. At the boiling-point, therefore, the aqueous tension takes the place of the whole barometric column, and is equal to the average air pressure. At  $121^{\circ}$  the aqueous tension is two atmospheres, at  $180^{\circ}$  it is ten atmospheres (see Appendix IV).

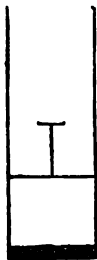
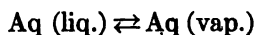


FIG. 54.

There is another standpoint from which these phenomena may be viewed. Water vapor can exist at  $10^{\circ}$  only if the pressure upon it is 9.1 mm. or less. If we imagine the water placed in a cylinder closed by a frictionless, weightless piston (Fig. 54), then at  $10^{\circ}$  the piston will remain at rest whether we place it high or low, provided it is loaded with a weight exactly equal to that of a layer of mercury 9.1 mm. thick covering its whole area.

We speak of such a system as being in **equilibrium** (see Chap. IX). With a less weight the piston will move slowly upwards, as the vapor continually given off by the water presses upon it, until it reaches the top or the water all evaporates. Conversely, if it bears a greater load, it will move down and the vapor will condense on the walls and bottom of the cylinder until the piston comes in contact with the

water itself and the vapor is all abolished. These conceptions will find constant application not only to physical but also to chemical phenomena. The expression:



is used to represent the state of equilibrium in a system like the above.

When water at a certain temperature has given the full amount of water vapor to the space above it that its aqueous tension permits, we say that the space is **saturated** with vapor. That **concentration** of vapor which constitutes saturation varies with the temperature of the water and depends therefore solely on the ability of the water to give off vapor. It has nothing to do with the size of the space, and is even independent of other gases the space may already contain. Thus, if a little air is first placed above the dry mercury (Fig. 53), causing it to fall, the *additional* depression produced by adding water is the same as if the air had been absent (p. 111).

**Water Vapor in the Air.** — The space immediately above the surface of the ground, which is mainly occupied by atmospheric air, is, on an average, less than two-thirds saturated with water vapor. That is to say, such air, when enclosed in a vessel containing water, will take up about one-half more than it already contains. The vapor of water at 100° in an open vessel displaces the air entirely and, if the required heat of vaporization is furnished, the liquid boils.

The water present in the air plays an important part in many chemical phenomena, as we shall see. All our substances and apparatus have traces of water condensed on their surfaces. This water is, in a sense, in an abnormal condition, for it does not evaporate even in dry air. It is observed to pass off in vapor, however, when we have occasion to heat the substance or apparatus.

**Water as a Solvent.** — One of those physical properties of water which are most used in chemical work is its tendency to dissolve many substances. This subject is so important and extensive that we shall presently devote a complete chapter to some of its simpler and more familiar aspects.

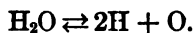
**Chemical Properties of Water.** — Water is so very frequently used in chemical experiments in which it is a mere mechanical adjunct, that the beginner has difficulty in distinguishing the cases in which it has itself taken part in the chemical interaction. The rather

limited list of kinds of chemical activity it can show should therefore receive careful notice:

1. Water is a relatively stable substance.
2. It combines with many oxides, forming bases or acids.
3. It combines with many substances, chiefly salts, forming hydrates.
4. It interacts with some substances in a way described as hydrolysis. This property will not be discussed until a characteristic example is encountered.

Perhaps we should add that steam at a high temperature oxidizes elements which readily combine with oxygen. For example, it turns iron into the magnetic oxide (p. 116). At such high temperatures, however, the water is partially resolved into a mixture of hydrogen and oxygen and, the latter being the more active of the two elements, the oxidizing effects predominate. Even other compounds containing oxygen will give exactly the same results. Hence this cannot be regarded as a property of water itself.

**Water a Stable Compound: Dissociation.** — In the case of a *compound*, the first chemical property to be given is always, whether the substance is **stable** or **unstable**. Usually, the specification is in terms of the temperature required to produce noticeable decomposition. Thus, potassium chlorate gives off oxygen at a low red heat. Now, water vapor, when heated, is partially decomposed into hydrogen and oxygen, yet, at 1882° only 1.18 per cent is broken up, and at 2000° the decomposition reaches only 1.8 per cent. When the temperature is lowered, the gases recombine to form water. Two arrows in the equation indicate that the action may proceed in either direction — is **reversible**:



A decomposition thus proceeds when the temperature is shifted in one direction (usually, though not always, upward), and reverses itself by recombination of the constituents when the temperature is displaced in the other direction (usually downward), is called a dissociation or a **thermal dissociation**. The decomposition of potassium chlorate (p. 83) is *not* a dissociation, because it is not reversible: oxygen gas will not, under any known circumstances, unite directly with potassium chloride.

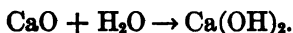
**The word unstable is frequently misused.** Thus, calcium chloride is sometimes said to be unstable, because, when exposed to the air, it takes up

moisture and finally dissolves in the water thus acquired. Or phosphorus trichloride is said to be unstable because it interacts with the moisture in the air, or ferrous sulphate is said to be unstable because it is oxidized by the oxygen in the air. Almost every substance, however, will undergo change readily, if a properly selected substance is allowed to come in contact with it. Quicklime, for example, is quickly slaked by water. According to this erroneous view practically every substance is unstable. Quicklime can be distilled, without decomposition, at the temperature of the electric arc, and is extremely stable. Stability refers solely to the effect of energy, usually in the form of heat, upon the substance, while the latter is carefully isolated from all other substances. The interactions of the substance with the components of the air, and with other reagents, must be recorded as separate chemical properties.

**Union of Water with Oxides.** — 1. Sodium oxide  $\text{Na}_2\text{O}$  unites violently with water to form sodium hydroxide:

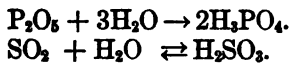


The slaking of quicklime is a more familiar action of the same kind:



No other products are formed. The clouds of steam produced in the second instance are due to evaporation of a part of the water by the heat produced in the formation of calcium hydroxide. The aqueous solutions of these two products have a soapy feeling, and turn red litmus blue (see Indicators), and the substances therefore belong to the class of alkalis or **bases**. Very many hydroxides which are of the same nature, for example ferric hydroxide  $\text{Fe}(\text{OH})_3$  and tin hydroxide  $\text{Sn}(\text{OH})_2$ , are formed so slowly by direct union of the oxide and water that they are always prepared in other ways. The oxides which, with water, form bases are called **basic oxides**.

2. Some oxides, although they unite with water, give **acids**, which are products of an entirely different character. Phosphorus pentoxide  $\text{P}_2\text{O}_5$  and sulphur dioxide  $\text{SO}_2$  (p. 88) are of this class and yield phosphoric acid and sulphurous acid, respectively:



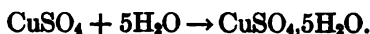
If the product is not volatile, it may be obtained by evaporating the excess of water. In the case of sulphurous acid, the above action is reversed by evaporation and the sulphur dioxide and water both pass off; in that of phosphoric acid, the white crystalline acid is obtained. In consequence of their relation to the acid, differing from it in *not*

containing the elements of water, these oxides are often called the **anhydrides** (Gk. *ἀν*, not, and *ὕδωρ*, water), of their respective acids. They are also called **acidic oxides**. The acids are sour in taste and turn blue litmus red.

These two classes of final products are so different that we make the distinction the basis of classification of the elements present in the original oxides. The elements, like sodium and iron, whose oxides give bases, are called **metallic elements**; those, like phosphorus, whose oxides give acids, are called **non-metallic elements**. The distinguishing words are selected because the division corresponds, in a general way at least, with the separation into two sets to which merely physical examination of the elementary substances would lead.

Formerly the hydroxides of metals were termed "hydrates," and the word is still used familiarly by chemists in a few cases, such as potassium "hydrate" KOH and sodium "hydrate" NaOH. These substances, however, have nothing in common with the compounds properly known as hydrates, whose nature is discussed in the next section.

**Hydrates.** — Many substances when dissolved in water and recovered by spontaneous evaporation of the solvent are found to have entered into combination with the liquid. The products, which are solids, are called **hydrates**. That they are regular chemical compounds is shown by the following two facts: (1) These compounds show definite chemical composition expressible by formulæ in terms of chemical unit weights (atomic weights) of the constituent elements. The proportions in solutions, and other physical aggregates, except by chance, cannot be expressed by means of formulæ. (2) A hydrate has physical properties entirely different from those of the water (or ice) and of the other substance used in preparing it. It is a typical compound, formed by the first variety of chemical change (p. 12). Thus, cupric sulphate, often called anhydrous cupric sulphate to distinguish it from the compound with water, is a white substance crystallizing in shining, colorless, needle-like prisms. The pentahydrate (blue-stone or blue vitriol) is blue in color, and forms larger but much less symmetrical (asymmetric or triclinic) crystals (Fig. 55):



Often much heat is given out in the formation of a hydrate. Thus, in the case of washing soda, the decahydrate of sodium car-

bonate  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , the heat of union (p. 99) is +8800 cal. This, however, does not in itself show that a chemical change has occurred. All chemical changes are accompanied by liberation or absorption of heat, but physical changes, like the condensation of steam and the freezing of water, and in many cases the dissolving of one substance in another, also involve the liberation of much heat.

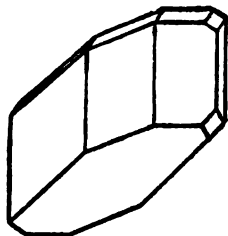


Fig. 55.

The **chemical properties** show hydrates to be relatively unstable. When heated, the hydrates, as a rule, lose none of the constituents of the original compound, but only those of the water in the form of water vapor. When melted, or when dissolved in water the hydrates are partly dissociated into water and the original substance. The aqueous solutions made from the anhydrous substances and from the hydrates have identical physical and chemical properties. Hence the cheaper of the two forms is generally purchased, and many of the chemicals used in laboratories are in the form of hydrates.

Since hydrates, when they decompose, usually give up water, we write their formulæ, *e.g.*,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , so that the water and the original substance are separated by a comma. A formula thus modified, so as to show some favorite mode of chemical behavior of the substance, is called a **reaction formula**. The formula  $\text{H}_{10}\text{CuSO}_4$ , which would show the same proportions by weight, is never employed, because its use would disguise the relation of the substance to cupric sulphate.

**The Dissociation of Hydrates: Efflorescence.**—The less stable hydrates dissociate very readily. Thus, the decahydrate of sodium sulphate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  (Glauber's salt), loses all the water it contains (**effloresces**) when simply kept in an open vessel. When kept in a *closed* bottle, a very little of it loses water, and then the decomposition ceases. The cause of this we discover when a crystal of the hydrate is placed above mercury, like the ice or water in Fig. 53 (p. 145). It shows an *aqueous tension* which we can measure. At 9° the value of this is 5.5 mm. As its temperature is raised, the tension increases. When the temperature is lowered, on the other hand, the tension diminishes, the mercury rises, and a part of the water enters into combination again. Different hydrates show different aqueous tensions at the same temperature. For example, at 30°, that of water

itself is 31.5 mm.; strontium chloride  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ , 11.5 mm.; cupric sulphate  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 12.5 mm.; barium chloride  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , 4 mm.

In view of these facts, we perceive that loss of water by efflorescence is like evaporation, excepting that it is a chemical decomposition and not a physical process. Those hydrates which, like Glauber's salt and washing soda  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , have a vapor tension approaching that of water itself, lose their water at ordinary temperatures at a rapid pace. In this connection we have to remember that atmospheric air is always less than two-thirds saturated with water vapor, and the partial pressure of this vapor *opposes the dissociation*, and tends to prevent the liberation of the water. Thus at  $9^\circ$ , the vapor tension of water being 8.6 mm., the average vapor pressure of water in the atmosphere will be about 5 mm. Any hydrate with a greater aqueous tension than 5 mm., at  $9^\circ$ , such as Glauber's salt, will therefore decompose spontaneously in an open vessel. But those with a lower vapor tension, such as the pentahydrate of cupric sulphate with a tension of 2 mm. at  $9^\circ$ , will not do so. Granular calcium chloride  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  is used for drying gases, because it has an exceedingly low tension of water vapor, and combines with water vapor to form  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ .

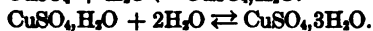
The behavior of hydrates does not indicate, as might seem at first sight to be the case, that the water is contained in them in some way in the free state. The fact is that the above statements, with corresponding changes in the wording, might be made of all dissociations in chemistry. Oxides which yield oxygen when heated give a different pressure of oxygen at each temperature, carbonates of carbon dioxide, and so forth.

The measurement of the vapor tension of hydrates gives definite information in regard to whether there are other hydrates, say of cupric sulphate, with less than the normal number of formula-weights of water. If there were only two substances,  $\text{CuSO}_4$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , with no compound of intermediate composition, then a partially decomposed specimen would be made up partly of the one substance and partly of the other. But if there were an intermediate compound, say  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ , then desiccating a specimen of the pentahydrate would give nothing but mixtures of  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  until all the latter was decomposed. Then, and only then, the trihydrate would begin to lose water. Now the trihydrate, being a definite and different substance, would have a vapor tension of its own, and experimental study would show its presence.

Experiment shows that there really are several hydrated cupric sulphates. The pentahydrate, at  $50^\circ$ , has a vapor tension of 47 mm., and this vapor tension is observed so long as any pentahydrate remains to be decomposed. As soon as the

proportion of water goes down to  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ , the vapor tension suddenly drops to 30 mm. As the desiccation continues, this tension is maintained until the composition has reached  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ . At this point the vapor pressure falls to that of the monohydrate, 4.5 mm., and remains at this value until all the rest of the water has been removed. Had there been no intermediate compound with  $3\text{H}_2\text{O}$  the tension would have dropped at once from 47 mm. to 4.5 mm. If, conversely, we try to combine water as vapor with anhydrous cupric sulphate, at  $50^\circ$ , a vapor pressure of at least 4.5 mm. is required to cause union to take place. The union stops when one formula-weight of water has undergone combination. To introduce more, the concentration of the water vapor must be increased to nearly seven times its first value, namely, to 30 mm. pressure. This enforces combination up to  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ . For further hydration, a still higher pressure of water vapor is needed (47 mm.), and the absorption ceases when  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  has been formed.

There are thus three distinct reversible actions which succeed one another as the hydration proceeds:



The first represents a greater affinity than the second, and the second than the third.

The graphic representation of these facts (Fig. 56) will make the behavior of the compounds clearer. The proportion of water combined with one formula-weight of cupric sulphate is laid off along the horizontal axis. The pressures at which it enters or leaves the compounds at  $50^\circ$  are the ordinates. As far as  $1\text{H}_2\text{O}$  the pressure is constant (4.5 mm.). Beyond that point and up to  $3\text{H}_2\text{O}$  it is constant but much higher. Between  $3\text{H}_2\text{O}$  and  $5\text{H}_2\text{O}$  it is constant again but higher still.

The tension of free water at the same temperature is 92 mm. It is constant irrespective of the amount of water, and would therefore be on a single continuous line parallel to the horizontal axis and twice as high above it as the uppermost

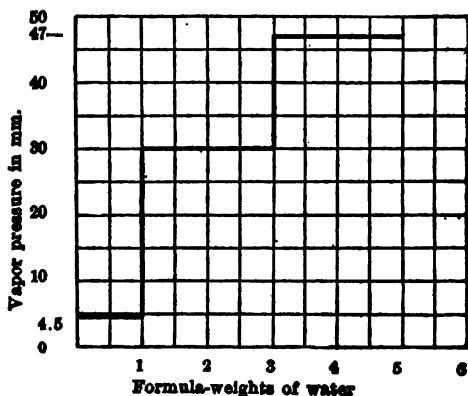


FIG. 56.

one in the diagram. If, at  $50^\circ$ , a vessel of water were put under a bell jar alongside of anhydrous cupric sulphate, its vapor would be more than sufficiently concentrated fully to hydrate the compound. Again, while 4.5 mm. pressure of water vapor will cause water to combine with anhydrous cupric sulphate at  $50^\circ$ ,



a pressure of 92 mm. will be required to liquefy the water vapor at the same temperature.

The above discussion shows that the last formula-weight of water, in hydrates which dissociate by stages, is not different in kind from the others. It differs only in the degree of tenacity with which it is held. It is therefore unnecessary, merely on this account, to dignify it by the separate, and misleading name of *water of constitution*, as has been done by some chemists.

Water of hydration is frequently called **water of crystallization**, on account of the fact that when water is driven off by heating, the substance usually crumbles to powder (*effloresces*). The term is decidedly misleading, however. It suggests that water and crystallization are related in some way, which is not the case. Sulphur, galena, potassium chlorate, and thousands of other crystallized substances, do not contain the elements of water. Nor do the substances which combine with water remain amorphous (without crystalline form) in its absence. They all crystallize from the molten condition or from some non-aqueous solvent, although, as substances different from the hydrates, their crystalline form is different. Iceland spar, or any other crystallized carbonate which can be decomposed by heating, becomes opaque and porous or falls to powder when the carbon dioxide is driven out. But it has not occurred to any one to call this carbon dioxide of crystallization! The fact is that all pure chemical substances, in solid form, when in a stable physical condition, are crystalline. Amorphous substances, like wax and glass, are always supercooled liquids.

The term arose from a misconception, and, when used, always succeeds in transmitting the misconception along with the name. The ease with which some of the hydrates decomposed suggested the idea that they contained water as a *discrete substance*. There is no more justification for this idea, however, than for the notion that carbonates contain ready-made carbon dioxide. The hydrates contain the elements of water just as sugar and alcohol do, and there is no evidence that they "contain water" in any other sense than that in which the phrase might be used of these organic bodies.

In consequence of their decomposition into and formation from substances capable of separate existence, the hydrates are classed with molecular compounds (*q.v.*). The behavior of the compounds of salts with ammonia (like  $2\text{AgCl}\cdot 3\text{NH}_3$ ), with nitric oxide, and with each other (double salts), is quite similar.

**How Formulæ and Equations are Obtained.**—In the last few pages several formulæ (*e.g.*, of hydrates) and several new equations have been given. How do we know what to set down in making an equation? We cannot learn this by simply writing formulæ on a piece of paper. In each case, experiments must be made in the laboratory. For example, how do we know that the common hydrate of cupric sulphate has the formula  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ , and not  $\text{CuSO}_4\cdot \text{H}_2\text{O}$ ? We must make a quantitative experiment. We weigh a porcelain dish or crucible, first empty, and then with a little of the

hydrate. Suppose the difference in weight to be 2.05 g. (= weight of hydrate). We then heat the dish and contents, until the water is driven out, and weigh again. The difference is now only 1.31 g. (wt. of anhydrous cupric sulphate). The water, therefore, weighed  $2.05 - 1.31 = 0.74$  g. Assuming that we know the formulæ (compositions) of cupric sulphate and of water, we obtain their formula-weights:  $\text{CuSO}_4 = 63.57 + 32.06 + 4 \times 16 = 159.63$ ; and  $\text{H}_2\text{O} = 2 \times 1.008 + 16 = 18.016$ . The formula must be  $\text{CuSO}_4, x\text{H}_2\text{O}$ . Also,

$$159.63 : x \times 18.016 :: 1.31 : 0.74.$$

Solving for  $x$  we have  $x \times 18.016 \times 1.31 = 159.63 \times 0.74$ , or  $x = 159.63 \times 0.74 / 18.016 \times 1.31 = 5.00$ . The formula is, therefore,  $\text{CuSO}_4, 5\text{H}_2\text{O}$ , and the equation for the decomposition:  $\text{CuSO}_4, 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 + 5\text{H}_2\text{O}$ .

To make an equation, we must note what substances are taken, and recognize by their properties all the substances produced. If all the substances are well known, and we can find their formulæ in a book, we can make the equation at once. If we cannot find the formulæ, we make measurements to determine the proportions by weight, calculate the formulæ, and then make the equation.

**Composition of Water.**—The measurement of the proportions by weight and volume in which hydrogen and oxygen combine to form water has been the subject of a larger number of elaborate investigations than any other single problem of this kind. The difficulty in making the former measurement arises from the fact that both constituents are gases, and are therefore difficult to weigh.

From 1842 until 1888, the accepted value of this proportion was that of the French chemist, Dumas. His experiments gave the ratio of hydrogen to oxygen 2 : 15.96, or  $2 \times 1.0025 : 16$ . Cooke and Richards (1888) obtained a figure for the oxygen appreciably smaller than this, namely 2 : 15.90, or  $2 \times 1.0063 : 16$ , and Lord Rayleigh (1889) 2 : 15.926. W. A. Noyes (1889–1907) made many determinations and, finally, from twenty-four measurements obtained the ratio 2 : 15.875, or  $2 \times 1.00787 : 16$ .

The investigation (lasting twelve years) which finally settled this question was that of Edward Morley. The most striking of his experiments consisted in a series of syntheses of water, in which he weighed the hydrogen as well as the oxygen, and afterwards weighed the water produced from them. The hydrogen was confined by absorption in palladium (p. 124), and could thus be contained in large quantity in a small, elongated bulb. During the progress of the experiment it was driven out by a suitable heating arrangement. The oxygen was contained in large globes holding 15–20 liters. The losses in weight of the

palladium tube and of the globes gave the hydrogen and oxygen consumed. The manipulator in which the gases were combined and the water collected is represented in Fig. 57. The gases entered through two small tubes marked A. Just above them, between two platinum wires, a discharge of electricity started the union and when necessary maintained it. The vessel was first filled by admitting oxygen, and the hydrogen was burned at the mouth of the tube from which it issued. This part of the apparatus was immersed in a vessel of water with transparent walls through which the union could be watched, and the steam formed was condensed and collected in the bottom of the vessel. The vacuum thus produced enabled the oxygen continually to flow into the manipulator from the globes. In this way forty-two liters of hydrogen and twenty-one liters of oxygen could be combined in about an hour and a half.

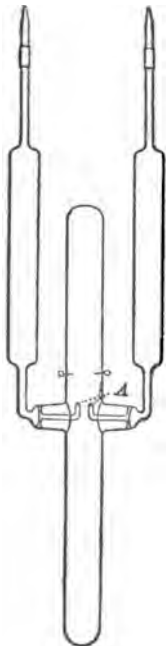


FIG. 57.

At the end of the experiment this part of the apparatus was disconnected and placed in a freezing mixture which converted the water into ice and practically condensed the whole of its vapor. The uncombined gas in the apparatus was withdrawn and its nature and quantity determined. The increase in weight of the manipulator gave the quantity of water formed. The success of each experiment could be tested by comparing the sum of the weights of oxygen and hydrogen with that of the water obtained from them. The manipulation was so skilful, and the various corrections used were so adequate, that this difference was almost negligible. The ratio of hydrogen to oxygen in water in this series of experiments was 2 : 15.879, a result which agreed with other methods of determining the same ratio which Morley used. It agrees also with the average of the numbers obtained by other observers.

The most probable value of the ratio by weight, taking his own and other trustworthy measurements into account, is given by Morley as 2 : 15.879, or 2.015 : 16. The proportion by weight at present accepted is 2 × 1.008 : 16. The proportion by volume is 2.0027 volumes of hydrogen to 1 volume of oxygen.

That the proportion by volume is very close to 2 : 1 may easily be shown. We may use a U-shaped tube closed at one end by a stopcock and graduated (Fig. 58). At first, the left limb of the tube, called a eudiometer, is filled with mercury. One of the gases is admitted so as to fill a portion of the tube and, the levels having been equalized (*cf.* p. 105), the volume of the gas is read. Then some of the other gas is introduced and the leveling and reading repeated. Let us suppose that 15 c.c. of hydrogen and 10 c.c. of oxygen have thus been taken.

The right limb is then filled with mercury and closed firmly with the thumb. A spark from an induction coil passing between the two short platinum wires near the top of the tube explodes the mixture. The steam produced by the union condenses almost immediately and occupies practically no volume worth considering. When the thumb is removed, the mercury rises on the left and fills up the space left by the disappearance of part of the gases. Unless the proportion taken happens to have been exact, some of one or other of the gases will remain. Its volume is measured by equalizing the levels and reading as before. In the case we have imagined, the residual gas is oxygen, and there are almost exactly 2.5 c.c. of it. It is evident, therefore, that 15 c.c. of hydrogen united with 7.5 c.c. of oxygen; in other words, the proportion by volume is 2 : 1.



FIG. 58.

**Gay-Lussac's Law of Combining Volumes.**—The almost mathematical exactness with which small integers express this proportion is not a mere coincidence. Whenever gases unite, or gaseous products are formed, the proportions by volume (measured at the same temperature and pressure) of all the gaseous bodies concerned can be represented very accurately by ratios of small in-



FIG. 59.

tegers. This is called **Gay-Lussac's law of combining volumes** (1808). Thus, when the above experiment is carried out at  $100^{\circ}$ , in order that the product, water, may be gaseous also, it is found that the three volumes of the constituents give almost exactly two volumes of steam. For example, 15 c.c. of hydrogen and 7.5 c.c. of oxygen give 15 c.c. of steam. Of course the hydrogen, oxygen, and steam must be measured at the same pressure, and the temperature must remain constant ( $100^{\circ}$ ) during the experiment. Proper manipulation secures the former, and a jacket filled with steam (Fig. 59) the latter condition. Strips of paper, 1, 2, and 3, are pasted on the jacket in such a

way that equal lengths of the eudiometer, in this case a straight one are laid off. The three divisions having been filled with a mixture of hydrogen and oxygen in the proper proportions, the gas, after the explosion, shrinks so as to occupy, at the same pressure, only two of the

From this universal truth in regard to the combination of gases we draw the important inference that the chemical unit-weights of simple substances, and the formula-weights of compounds, in the gaseous condition, occupy at the same temperature and pressure volumes which are equal or stand to one another in the ratio of small integers (see Molar weights).

The chemical behavior of the other compound of hydrogen and oxygen, hydrogen peroxide (*q.v.*), is difficult to comprehend until further experience has been gained. Then, too, its formula  $H_2O_2$  cannot be justified until the means of determining molar weights in solution have been discussed. In view of the facts, it will be taken up later.

**Exercises.** — 1. Name some other transitions from one physical state to another which are familiar (p. 144).

2. What evidence is there in the common behavior of ether and chloroform to show that these liquids have high vapor tensions?

3. If the pressure of the steam in a boiler is ten atmospheres, at what temperature is the water boiling (p. 146)?

4. How many grams of water could be heated from  $20^\circ$  to  $100^\circ$  by the heat required to melt 1 kgm. of ice at  $0^\circ$ ?

5. What do you infer from the fact that alum and washing soda lose their water of crystallization when left in open vessels, while gypsum does not (p. 152)?

6. Which facts show most conclusively that hydrates are true chemical compounds?

7. In what ways does a hydrate differ from, (a) a solution, (b) an hydroxide?

8. Should you expect to find any difference, in respect to chemical activity, between the three forms of water (ice, water, and steam)? If so, arrange them in the order of probable increasing activity (pp. 93–94). Have we had any experimental confirmation, or the reverse, of this conclusion?

9. Which contains more internal energy, and is therefore more active, the anhydrous substance, or the corresponding hydrate?

10. Gypsum is a hydrate of calcium sulphate  $CaSO_4$ . If 6 g. of gypsum, when heated, lose 1.256 g. of water, what is the formula of the hydrate?

11. At what temperature will ice melt in a vacuum?
12. Indicate briefly the objections to the *form* of statement (commonly used): "Blue vitriol loses 4 molecules of water of crystallization at 100° and the fifth at 200°." Re-write this correctly.
13. Equal weights (say, 249.7 g.) of blue-stone and of  $\text{CuSO}_4$  are enclosed at 50°, occupying the whole volume. Find the composition of the system at equilibrium.

## CHAPTER IX

### RELATIONS BETWEEN THE STRUCTURE AND BEHAVIOR OF MATTER. THE KINETIC-MOLECULAR VIEWPOINT

WE have seen (p. 65) that matter is composed of minute particles called **molecules**. Just as we can thoroughly understand the behavior of a watch or an automobile engine only if we know the details of its structure, and how the parts work, so we can understand the physical and chemical behavior of matter in masses only if we are familiar with its ultimate mechanism. Hence, we must now take up the structure of matter in its three states, the gaseous, the liquid, and the solid. In doing this, we shall keep constantly in view the connection between the molecular relations and the general behavior of the matter.

**The Molecular Structure of Gases.** — The most noticeable fact about gases is that they *can be compressed* to an enormous extent. Oxygen at 760 mm., for example, can be reduced by pressure to one two-hundredth of its volume, or even less. The compression does not affect the individual molecules, and therefore does not diminish the volume actually occupied by the oxygen, but crowds the molecules closer together and *diminishes* to one two-hundredth **the space** between them. Compressing a gas is, in fact, mainly reducing the *empty space* of which it chiefly consists. To understand what follows, the reader must keep constantly and vividly before him a mental image of a jar of gas as consisting of small particles separated by relatively wide, empty spaces. The molecules are in rapid motion and move in straight lines, excepting when they strike one another or the wall of the vessel, and rebound.

The actual number of molecules in a given volume of a gas will be discussed in Chapter XII, where the figures can be given in a more memorable form.

**The Qualitative Properties of Gases.** — Let us now note the more obvious qualities of gases, printing in *italics* the *fact concerning a mass of gas*, and in **black type** the property of the molecules which accounts for the fact.

The most remarkable thing about a gas, considering the looseness with which its material is packed, is the total *absence* in it of any tendency to *settling* or subsidence. Since the molecules cannot be at rest upon one another, as the great *compressibility* shows, we are driven to suppose that they are **widely separated from one another**, and that they occupy the space by constantly moving about in all directions. But a moving aggregate of particles which *does not* even finally *settle* must be in **perpetual motion**. We must, therefore, imagine the molecules to be wholly unlike visible particles of matter in having **perfect elasticity**, in consequence of which they undergo no loss of energy after a collision. They must continually strike the walls of the vessel and one another and rebound, yet without loss of motion. The fact that each gas is *homogeneous*, efforts to sift out lighter or heavier samples having failed, requires the supposition that **all the molecules of a pure gas are closely alike**.

The *diffusibility* of gases is due to the **motion of the molecules**, and their *permeability* to the **space** available to receive molecules of another gas. These two modes of behavior involve no additional molecular properties. The word "diffusion" is often thought to mean the property of a given mass of gas in virtue of which another gas can mix with the given mass. This property is not diffusibility but permeability. It is the motion of each gas, making its way into the other gas, which is diffusion. Diffusion is spontaneous motion of the parts of a gas *away from* their original location. Unless this motion is into an empty space, the diffusing molecules must, of course, move into another body of gas. In the case of the jars of carbon dioxide and air (p. 125), each gas moved in part *out of* its original jar (diffused), and each received parts of the other gas *into* its jar (was permeated).

### **Quantitative Properties of Gases: Boyle's and Charles' Laws.**

— Passing now to Boyle's law (p. 106), the thing to be accounted for is that when a sample of a gas diminishes in volume, its pressure increases in the same proportion. Let the diagram (Fig. 60) represent a cylinder with a movable piston, upon which weights may be placed to resist the pressure. Now the pressure exercised by the gas cannot be explained as being like the pressure of the hand upon a table, since we have just assumed that the particles are not even approximately at rest, and the spaces between them are enormous compared with the size of the molecules themselves. The

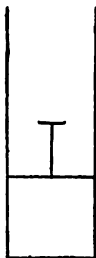


FIG. 60.



gaseous pressure must therefore be attributed to the colossal hailstorm which their innumerable impacts upon the piston produce. If this is the case, the compressing of a gas must consist simply in moving the partition downwards so that the particles as they fly about are gradually restricted to a smaller and smaller space. Their paths become on an average shorter and shorter. Their impacts upon the wall become more and more frequent. So the pressure which this occasions becomes greater and greater, and is proportional to the degree of crowding (the **concentration**) of the molecules.

There are two other points which must be added. When we diminish the volume to one-half, we find from experience that the pressure becomes exactly, or almost exactly, twice as great. This must mean that although the particles are becoming crowded they do not interfere with one another's motion, excepting of course where actual collision causes a rebound. Only in the absence of interference would doubling the number of particles per unit of volume give exactly double the number of impacts on the walls. Hence the particles must have practically no tendency to cohesion. Again, the molecules must move in straight lines, because, if they moved in orbits of some kind, many of the orbits would not be intersected by the wall of the vessel until great reduction in the volume had taken place, and thus, as the volume diminished, the frequency of the impacts, and therefore the pressure, would increase faster than the concentration.

Boyle's law therefore adds four more conceptions to our molecular hypothesis, namely, that the **impacts of the molecules** produce the *pressure*, that the **crowding of the molecules** represents the *concentration* (p. 103), and that the particles **move in straight lines** and **show almost no cohesion**, since *pressure and concentration are very closely proportional to one another*.

It will be seen, on consideration, that if the molecules are assumed to repel one another, they would do so more violently the more closely they were packed together. This assumption would therefore suit the case of a gaseous body in which the pressures increased according to some power of the concentration other than the first, and therefore much more rapidly than in known gases. In spite of its inapplicability, this notion is supposed by many people to be part of the kinetic theory.

*Charles' law* (p. 110), that a gas receives equal increments in volume or pressure for equal elevations in temperature, requires but one addition to the hypothesis. Concretely, if our specimen of gas (Fig. 60) is

at  $0^{\circ}$ , and we permit its pressure to remain constant by leaving the same weight on the piston, then when the temperature of the gas is raised to  $1^{\circ}$ , the volume will gain  $\frac{1}{273}$  of the original volume. If, on the other hand, we restrict the gas to the original volume, the pressure will evidently increase, and the augmentation will be  $\frac{1}{273}$  of the original pressure. Now, how can we account for an increase in pressure as the result of heating a mass of rapidly moving molecules? The action of a particle colliding with a surface is measured in physics in terms of its mass and its velocity. It is evident that *heating* a cloud of molecules would not increase the mass of each, and it must therefore *increase the velocity of each*, since the kinetic energy of all becomes greater. This conclusion is in harmony with our experience that violently rubbing a solid raises its temperature, and such a mode of treatment might plausibly be supposed to communicate motion to the minute parts of the body.

**Gay-Lussac's and Avogadro's Laws.** — The fact that the *combining volumes of gaseous substances are equal, or stand to one another in the ratio of small whole numbers* (cf. p. 157), suggests two ideas: First, that chemical combination, considered in detail, and arranged to harmonize with this theory, would involve *unions of a few particles of more than one kind to form composite molecules*.\* And, second, that a simple integral relation must be assumed to exist between the *numbers of molecules in equal volumes of different gases*, at the same temperature and pressure. Avogadro (1811), the professor of physics in Turin, put forward the hypothesis that these numbers *might be equal*. A more strict study of the assumptions we have been making, and of some additional facts, has since shown that no other conjecture than Avogadro's would be consistent with them. Thus it now bears the relation of a logical deduction from the kinetic-molecular theory and the properties of gases, and is known as **Avogadro's law**. It may also be put in the form: **At the same temperature and pressure, the molecular concentration** (cf. p. 104) **of all kinds of gases has the same value.**

**Diffusion.** — The *law of diffusion* (p. 126) harmonizes with the kinetic-molecular theory without further modification of the latter. The strict deduction of this law, as well as of the preceding ones, from

\* This is essentially the idea used by Dalton (p. 65), before Gay-Lussac's law was known, however, for the explanation of the laws of chemical combination.

our series of assumptions, will be found in any work on physical chemistry.

The speed of the hydrogen molecule at room temperature is 1840 meters per second. The masses of the hydrogen and oxygen molecules are as 1 : 16, and the speeds of diffusion (p. 126) as  $\sqrt{16} : \sqrt{1}$ , or 4 : 1. Hence the speed of the oxygen molecule is one-fourth of 1840, or 460 m. per sec.

Calculation shows the activity of the molecules to be so great that, in air, the number striking a single square centimeter of surface every second would fill no less than twenty liters.

**Two Deviations from Boyle's Law.** — Finally, we have referred (p. 108) to the fact that at *low pressures the concentration increases more, and at high pressures much less* than Boyle's law indicates. The former effect is brought into accord with our hypothesis when we remember that the matter even of gases can *cohere*, as is shown plainly when gases are solidified. The tendency of the molecules to cohere must therefore show itself in the gaseous condition by pulling the gas together and producing somewhat greater concentration than is strictly consistent with the value of the pressure. Thus, 2 liters of oxygen at 760 mm. and 0°, when subjected to 2 atmospheres pressure, give 0.9991 liters instead of 1 liter. The additional contraction of 0.0009 liters (0.9 c.c.) is due to the effect of the cohesion when the molecules are thus crowded closer together. The gases which are more easily liquefied than is oxygen show greater effects. Thus, 2 liters of sulphur dioxide at 760 mm. and 0°, when subjected to 2 atmospheres pressure, give only 0.974 liters, showing a contraction due to cohesion of 26 c.c. At temperatures below 0° the contractions due to cohesion become rapidly greater. This cohesion is not of the nature of gravitational attraction. Although this effect of cohesion is usually insignificant, the modern method of liquefying gases (*q.v.*) depends upon it almost entirely.

The abnormally small reductions in volume which occur when the volume of the gas has already been greatly reduced remind us that, according to our hypothesis, it is **only the space between the molecules that is diminished** as pressure rises, and not the space **occupied by the molecules**. Hence, when the molecules have become so crowded together that this irreducible space begins to form an appreciable fraction of the whole, a doubling of the pressure will diminish to one-half its value only a **part** (the vacant part) of the volume the gas occupies.

If the incompressible space occupied by the molecules is called  $b$ , and that of the whole gas  $v$ , then the amended form of Boyle's law reads  $p(v - b) = \text{constant}$ . Similarly, if the cohesive tendency is taken into account, it is plain that its effect will be numerically greater at small volumes, although not so easily observed. It is in fact inversely proportional to the square of the volume. If it is expressed in the same units as the pressure by  $a$ , the total of the compressing tendencies becomes  $p + \frac{a}{v^2}$ . Hence Boyle's law, for constant temperatures, as amended by

van der Waals, reads  $\left(p + \frac{a}{v^2}\right)(v - b) = \text{constant}$ , a formula which describes

the actual behavior of most gases with remarkable accuracy. Hydrogen alone, at ordinary temperatures, shows no excessive compressibility at low pressures. Thus, 2 liters of hydrogen at 760 mm., when subjected to 1520 mm. pressure, give 1.0006 liters, or 0.6 c.c. more than Boyle's law suggests. The cohesion ( $a$ ) is here negative, so that the effect of the constant ( $b$ ) prevails from the very first.

It will be noted that the kinetic theory affords a mechanical explanation (*i.e.*, description in detail) of all the properties of gases, with the exception of the cohesion. It includes no machinery for explaining how the attraction operates.

In consequence of these two deviations, there are not *exactly* equal numbers of molecules in equal volumes of any two different gases, at the same temperature and pressure. An imaginary gas, which exhibits neither deviation, called a **perfect gas**, is often referred to in discussing the behavior of gases.

**Summary.** — We may now summarize the principal facts about gases in mass, appearing in italics above, with the corresponding features of the molecular relations, in heavy type, which we have added one by one.

FACTS ABOUT GASES IN MASS.	CORRESPONDING RELATIONS OF MOLECULES.
Compressibility . . . . .	Vacuum + molecules widely separated.
Diffusibility . . . . .	Molecules in rapid motion.
Permeability . . . . .	Empty space relatively large.
Non-settling . . . . .	Molecules perfectly elastic.
Homogeneity . . . . .	Molecules of any one substance closely alike.
Pressure . . . . .	Due to impacts of molecules.
Boyle's law . . . . .	Pressure proportional to concentration of the molecules. Molecules move in straight lines and, when widely scattered, show almost no tendency to cohesion.

FACTS ABOUT GASES IN MASS.	CORRESPONDING RELATIONS OF MOLECULES.
Dalton's law (p. 111) . . . . .	Nothing new.
Henry's law . . . . .	Nothing new.
Charles' law . . . . .	Rise in temperature increases the velocity, and therefore the kinetic energy of the molecules.
Gay-Lussac's law and above and other facts.	There are equal numbers of molecules in equal volumes of different gases at the same temperature and pressure (Avogadro's law).
Law of diffusion.	Nothing new.
Abnormal compressibility, especially at low pressures.	The tendency to cohesion gives measurable, though slight effects.
Abnormal incompressibility, especially at high pressures.	The molecules themselves are incompressible.

**Critical Temperature.** — When the concentration of a gas at ordinary temperatures is greatly increased by compression, the cohesive forces have an opportunity to produce liquefaction. In many cases, as with sulphur dioxide and carbon dioxide, when the approximation of the molecules has reached a certain point, the liquid begins to form on the sides of the vessel. The condition is then exactly the same as that of aqueous vapor and water (p. 145), and no further increase in pressure is required to complete the liquefaction of the whole. The *only* difference between steam, at a pressure below the aqueous tension of water at 10°, and carbon dioxide at the same temperature, is that not more than 9.1 mm. of pressure is required to liquefy the steam, while about 50 atmospheres are needed to liquefy the carbon dioxide.

There are some gases in which, at the ordinary temperature, even with the closest approximation of the molecules, the cohesion is unable to overcome the motion of the molecules and draw the material together into the more compact liquid form. Such gases are hydrogen, oxygen, nitrogen, and air, which is a mixture of the last two. The remedy is obvious. We know of no way to increase the intrinsic cohesiveness of the material, but we can reduce the kinetic energy of the molecules by lowering the temperature of the gas. When this has been done sufficiently, compression is followed by liquefaction. Now it is found that there is a critical value for each individual gas, to or beyond which the kinetic energy must be reduced by lowering the temperature, before the cohesive tendency of that particular gas can become effective to produce liquefaction. In 1869 Andrews found

that carbon dioxide could be liquefied at  $0^{\circ}$  by 38 atmos. pressure, and at  $30^{\circ}$  by 71 atmos., but that above  $31.35^{\circ}$  it could not be liquefied by any pressure. He discovered that each gas has a **critical temperature**, as he called it. For carbon dioxide, this temperature can be observed by placing a heavy walled, glass tube (Fig. 61), half-filled with liquid carbon dioxide, in a beaker of water, and gradually raising the temperature of the latter. At  $31.35^{\circ}$ , the surface between the liquid and gas becomes hazy and vanishes. The vapor pressure in the gas has become so great that the gas has, at this point, the same density as the liquid. When the temperature falls once more, the surface reappears at  $31.35^{\circ}$ .

For oxygen this temperature is  $-118^{\circ}$ , for hydrogen  $-234^{\circ}$ , for nitrogen  $-146^{\circ}$ . For carbon dioxide it is  $31.35^{\circ}$ , for sulphur dioxide  $156^{\circ}$ , for water  $358^{\circ}$ . The temperature of a room being below the critical points of the last three substances, they are all liquefiable without cooling, and more easily the farther the ordinary (say  $20^{\circ}$ ), lies below the critical temperature.



FIG. 61.

**History of the Kinetic-Molecular Theory.**— This theory was first suggested by Daniel Bernoulli (1738), who explained by its means the pressure and compressibility of gases. Lomonossov (1748) developed the theory very completely and explained Boyle's law and the effects of changes in temperature by means of it. He also anticipated from the theory the existence of the second deviation from the law of gases (1749), a discovery usually credited to Dupré (1864). He likewise pointed out that there was no limit to the maximum velocity of a molecule, and therefore no upper limit of temperature, but that there must be a lower limit (the absolute zero) at which the molecules would be at rest (1744). This work was entirely forgotten, until attention was called to it in 1904 by Menshutkin.

Similar views were formulated in detail by Waterston (1845), but were still so much ahead of the time that the committee of the Royal Society did not approve the paper for publication, and it was discovered in the archives of the society, long afterwards, by Lord Rayleigh. The development of the theory, so far as it applies to heat is therefore usually credited to Joule (1855-60) and, in respect to all properties of gases, to Krönig (1856) and Clausius (1857), who knew nothing of the earlier work.

**Molecular Relations in Liquids.**— The fact that even great pressures produce little diminution in the volume of a liquid shows that the **free space**, present in gases, is **absent in liquids**. The measured effects of various pressures show, for example in the case of water, that to reduce the volume to one-half would require, not doubling the pressure as in a gas, but increasing it from 1 to 10,000 atmospheres. The molecules of a liquid are actually in contact with one another, and are themselves compressible, though with difficulty (Richards).

The phenomena connected with surface tension, such as coherence into drops, show that **cohesion** plays a larger part in liquids than in gases.

We are further compelled to suppose that there is **motion of the molecules inside the liquid**. When alcohol, as the lighter liquid, is floated upon water in a cylinder (Fig. 62), the plane separating the liquids is at first easily visible. But soon it becomes obliterated. The water diffuses upward, and the alcohol downward, each sifting its way through the other in spite of gravity. The complete mixing of the liquids takes a very much longer time than in the case of two gases. It may take months. But even here the hypothesis helps us, by pointing to the vast impediment which the close packing of, and therefore enormous friction between the molecules must place in the way of the progress of any one molecule. Further, once the mixture is formed, no tendency to spontaneous separation is ever observed. Here again, the hypothesis shows that none is to be expected. If it occurred, it would be immediately undone by diffusion.

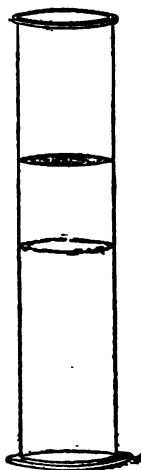


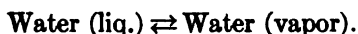
FIG. 62.

**Molecular Relations of Liquid and Vapor.**— When the water was introduced above the barometric column (Fig. 53, p. 145), the escape of vapor, that is, of part of the liquid in gaseous form, could have resulted only from the spontaneous motion of the molecules in the liquid. Some of the molecules, moving near the surface, went off into the space above the water and became gaseous. To be consistent, we must also conclude that the vapor above the water is not composed of the *same* set of molecules one minute as it was during the preceding minute. Their motions must cause many of them to plunge into the liquid, while others emerge and take their places. When the water is first introduced, there

are no molecules of vapor in the space at all, so that emission from the water predominates. The pressure of the vapor increases as the concentration of the molecules of vapor becomes greater, hence the mercury column falls steadily. At the same time the number of gaseous molecules plunging into the water per second must increase in proportion to the degree to which they are crowded in the vapor. The rate at which molecules return to the water thus begins at zero, and increases steadily; the rate at which molecules leave the water, however, maintains a constant value, because the properties of the water are not affected by changes in the concentration of the vapor. Hence the rate at which vapor molecules enter the water must eventually equal that at which other molecules leave the liquid. At this point, occasion for visible change ceases and the mercury comes to rest. We are bound to think, however, of the exchange as still going on, since nothing has occurred to stop it. The condition is not one of rest, but of rapid and equal exchange. Such, described in terms of the theory, is the state of affairs which is characteristic of a condition of **equilibrium** (p. 146). The condition is kinetic, and not static.

**Equilibrium.** — This term is used so often in chemistry, and is used in so unfamiliar a sense, that the reader should consider attentively what it implies. Three things are characteristic of a state of equilibrium:

1. There are **always two opposing tendencies** which, when equilibrium is reached, balance each other. In the foregoing instance, one of these is the hail of molecules leaving the liquid, which is constant throughout the experiment. It represents the **vapor tension of the liquid**. The other is the hail of returning molecules, which, at first, increases steadily as the concentration of the vapor becomes greater. This is the **vapor pressure of the vapor**. These have the effect of opposing pressures and, when the latter becomes equal to the former, **equilibrium** is established. In all cases of equilibrium we shall symbolize the two opposing tendencies by *two* arrows, thus:



2. Although their effects thus neutralize each other **at equilibrium, both tendencies are still in full operation**. In the case in point, the opposing hails of molecules are still at work, but neither can effect any visible change in the system. Equilibrium is a state, not of rest, but of balanced activities.



3 (and this is the chief mark of equilibrium). **A slight change in the conditions produces, seldom a great or sharp change, but always and instantly, a corresponding small change in the state of the system.** The change in the conditions accomplishes this by **favoring or disfavoring one of the two opposing tendencies.** Thus, for example, when the *temperature* of a liquid is *raised*, the kinetic energy of its molecules is increased, the rate at which they leave its surface becomes greater, the vapor tension increases and, hence, a greater concentration of vapor can be maintained. The system, therefore, quickly reaches a new state of equilibrium in which a higher vapor pressure exists. A heap of matter on a table is not in equilibrium, because addition of more material produces no response until, when a very great quantity is added, the table breaks. But a body on the scales is in equilibrium, for the addition of the smallest particle produces a corresponding inclination of the beam.

In the preceding illustration, the evaporating tendency was *favoured* by a rise in temperature. As an example of a change in conditions *disfavoring* one tendency, take the case where the liquid is placed in an *open*, shallow vessel. Here the condensing tendency is markedly discouraged, for there is practically no return of the emitted molecules. Hence complete evaporation takes place. Elevation of the temperature hastens the process. A draft insures the practical prevention of all returns, and has therefore the same effect. The two methods of assisting the displacement of an equilibrium, and particularly the second, in which the opposed process is weakened and the forward process triumphs solely on this account, should be noted carefully. They are applied with surprising effectiveness in the explanation of chemical phenomena (see Chaps. XV and XVIII).

**Molecular View Applied to Solids.** — The properties of solids differ from those of liquids chiefly in the fact that the solid has a *definite form* of which it can be deprived only with difficulty. This we may explain in accordance with the kinetic theory by the supposition that the **cohesion in solids is very much more prominent** than in liquids. We obtain solids from liquids by cooling them; in other words, by diminishing the kinetic energy and therefore the velocity of the particles. The cohesive tendency of the latter is thus able to make itself felt to a greater extent. If, conversely, we heat a solid, or, according to the hypothesis, if we increase the speed with which the particles move, the body first melts and gives a liquid, and this finally

boils and becomes a gas. The intrinsic cohesion of the particular substance can undergo no change, but the increasing kinetic energy of the particles steadily and continuously obliterates its effects. Yet *some motion still survives in a solid*. Thus we find that when the layer of silver is stripped from a very old piece of electroplate the presence of this metal in the German silver or copper basis of the article is easily demonstrated.

Roberts Austen has found that if bars of lead are prepared, in one end of which an alloy containing a certain proportion of gold has been used, while the remainder of the bar is composed of pure lead, the gold has a tendency to wander slowly into the pure lead. The process is greatly aided by keeping the bars at a fairly high temperature, but one much below the melting-point is amply sufficient. After a suitable interval of time the bar may be sawn into fragments of equal length, and its parts analyzed. The quantity of gold in a section is found to increase as we approach the portion of the bar to which originally the whole of the gold was confined.

The tendency of all solids to assume crystalline forms, which show definite *cleavage* and other evidences of **structure**, distinguishes them sharply from liquids (see Crystal structure). The force of cohesion in liquids is exercised equally in different directions. In solids it must differ in different directions in order that structure may result. Since each substance shows an individual structure of its own, these directive forces must have special values in magnitude and direction in each substance.

**Crystallization.** — A crystal arises by growth. When the process is watched, as it occurs in a melted solid or an evaporating solution, the slow and systematic addition of the material in lines and layers, as if according to a regular design, is one of the most beautiful and interesting of natural phenomena. The fern-like patterns produced by ice on a window-pane show the general appearance characteristic of crystallization in a thin layer. A larger mass in a deep vessel gives forms which are geometrically more perfect. From its very incipency the crystal has the same form as when, later, its outlines can be distinguished by the eye. Hence the outward form is only an expression of a specific internal structure which the continual reproduction of the same outward form on a larger and larger scale leaves as a memorial of itself in the interior.

**Crystal Forms.** — Crystalline form is so continually used in identifying (p. 40) the substances produced in chemical actions that

a list of the kinds of forms which occur will assist in giving definite meaning to our descriptions.

The classification of crystalline forms is carried out according to the degree of symmetry of the crystals. Thirty-two distinct classes are distinguished, but for our purpose a rougher division into six groups will suffice. These groups are known by the following names:

- |                             |   |
|-----------------------------|---|
| 1. Regular system.          | 5. Monosymmetric, or monoclinic system. |
| 2. Square prismatic system. | 6. Asymmetric, or triclinic system.     |
| 3. Hexagonal system.        |   |
| 4. Rhombic system.          |   |

The **regular system** presents the most symmetrical figures of all. Some forms which commonly occur are the octahedron (Fig. 63) shown by alum, the cube (Fig. 64) affected by common salt, and the dodecahedron (Fig. 65) frequently assumed by the garnet.

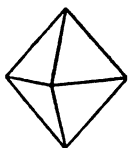


FIG. 63.

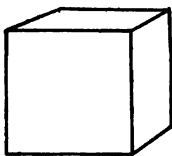


FIG. 64.

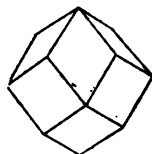


FIG. 65.

The **square prismatic system** includes less symmetrical forms than the previous one, since the crystals are lengthened in one direction. Fig. 66 shows the condition in which zircon  $\text{ZrSiO}_4$ , which furnishes us with the basis of certain incandescent illuminating arrangements, occurs in nature. The form of ordinary hydrated nickel sulphate  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  is similar to this.



FIG. 66.



FIG. 67.



FIG. 68.

The **hexagonal system**, like the preceding, frequently exhibits elongated prismatic forms, but the section of the crystals is a hexagon instead of a square, and the termination is a six-sided pyramid. Quartz (Fig. 67), or rock crystal, is the most familiar mineral in this system. Calcite ( $\text{CaCO}_3$ ), which is chemically identical with chalk,

or marble, takes forms known as the scalenohedron (Fig. 68) and rhombohedron (Fig. 69), which are classified in a subdivision of this system. Indeed, recently it has become common to erect this into a separate system (the trigonal), in which both quartz and calcite are included.

The **rhombic system** includes the natural forms of the topaz, and of sulphur (Fig. 8, p. 14), as well as those of potassium permanganate (Fig. 70), potassium nitrate (Fig. 71), and many other substances. These crystals exhibit a good deal of symmetry, but their section is always rhombic, and hence the name.

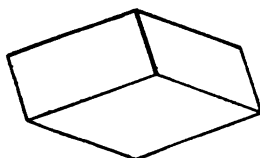


FIG. 69.

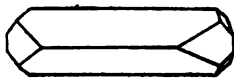


FIG. 70.



FIG. 71.

The **monosymmetric system** exhibits forms which have but one plane of symmetry. Gypsum (Fig. 72), which is hydrated calcium sulphate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and felspar (Fig. 3, p. 5) are minerals possessing forms of this kind. Tartaric acid, rock candy (Fig. 73), potassium chlorate, and hydrated sodium carbonate (washing soda) belong to this system.



FIG. 72.

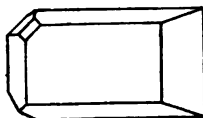


FIG. 73.

The **asymmetric system** includes forms which have no plane of symmetry whatever. Blue vitriol (Fig. 55, p. 151),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , is one of the most familiar substances of this kind.

The forms of crystals which we may actually make seldom correspond exactly with the figures. If we allow a crystal to grow upon the bottom of a vessel, for example, it will usually have a tendency to spread itself out parallel to the surface of the glass, and when taken up for examination, will be found to present a somewhat distorted form. By changing, at frequent intervals, the face on which the

crystal stands, however, uniform growth in all directions is secured. Hanging a small crystal by a thread insures almost ideal development. Yet the form even of distorted crystals can readily be recognized by suitable means. The shape of the faces may indeed be extremely misleading. We find, however, that the angles at which the faces meet are always the same, whatever disproportionate growth may have occurred in the development of the crystal.

Since, in general, each substance has a form of its own, no other substance, as a rule, can be used even partially in building up the crystal (see, however, Isomorphism). This fact is taken advantage of in order to separate chemical substances from impurities. The impure body is first dissolved in some solvent. The preponderating substance in the mixture, unless it is very much more soluble than the impurity, will then usually give pure crystals while the foreign body remains in solution.

The shapes of gems must not be confused with crystalline forms. The original crystals are cut and polished to a new form specially adapted to increase the ornamental value of the stone by causing it to reflect more light (see Diamond). Again, glass is really a very viscous fluid (amorphous body, p. 154), and has no structure or form of its own. The word "crystal" applied to cut glass would therefore be misleading if taken literally.

**Crystal Structure.** — As the above would lead us to expect, the study of crystallized substances shows that their peculiarities are not confined to the outside layer. The outline represents a certain structure which permeates the whole mass. In crystals of the regular system, many of the ordinary physical properties are the same as those of an amorphous substance, like glass. For example, if we turn a sphere out of crystallized salt and hang it in pure water, we find that solution takes place at a uniform rate all over the surface. This is not the case, however, with substances from any of the other systems. Spheres cut from substances belonging to the second and third systems would dissolve more, or less, rapidly in the direction of the chief axis than in any other direction, and so ellipsoids of revolution would quickly be produced. In the other three systems, more complex forms would result.

The tenacity of crystals, to whatever system they may belong, is different in different directions. Thus, a crystal of salt has a cleavage parallel to any of the faces of the cube, and, therefore, splits most easily in one of three directions at right angles to each other. Calcite, whatever the outward form of the crystal, always cleaves so as to give a rhombohedron. Fluorite  $\text{CaF}_2$ , although almost always cubical in form, splits when broken so as to give an octahedron.

The behavior of crystals towards light is also extremely interesting. The rate at which light moves through crystals of the regular system is the same in all

directions. In other crystals, however, we find that it moves with a different speed in different directions, the variations in speed being likewise related to the outward form. Finally, if a thin slab of rock salt is covered with wax and the point of a heated cone of metal is placed in the center, the wax melts uniformly in a circle around the point, indicating that the heat is conducted with equal speed in all directions. The way in which the slab has been cut with reference to the surface of the crystal, in the case of substances of the first of the above systems, has no effect upon this result. In all other cases, however, the zone of melting wax is in general elliptical, or even more complex in form, according to the system to which the substance belongs and the direction in which the slab has been cut (see Chap. XXII).

***Practical Value of the Molecular Viewpoint.***—The value of the kinetic-molecular viewpoint has been illustrated above, and will appear again when we deal with solutions and chemical equilibrium. But indeed its field of application is coextensive with the science itself.

The conceptions of the kinetic theory are of especially great assistance in rationalizing chemical manipulation and so hastening the acquisition of an intelligent control of it. The constructive imagination, on the use of which experimental work depends so much for its success, must have something to work with, and this view furnishes a tool such as it requires. Methods taught by rule of thumb are slowly learned and constantly fail in application. We may be told a dozen times that using reagents in finely powdered, or metals in granulated condition hastens all interactions, and still never think of this abstraction when working. But if it is suggested that, in terms of the kinetic theory, molecules must meet freely in the same medium to react easily, and that, therefore, the larger the surface the more copious will be the supply of molecules dissolving, we are likely to form a conception of the reason for the procedure that will be lasting.

When a student is told to concentrate a solution and set it aside to crystallize, why does he evaporate the liquid rapidly to dryness, and still expect the residue to appear in large, well-formed crystals? Because he has no notion of the necessary slowness of the process of crystallization. But if he has the idea that it is like building a house, one stone at a time, and that there are far more units to be laid down according to plan in making the smallest visible crystal than there are bricks in building the largest factory, his procedure may promptly become more rational.

**Stochastic Hypotheses.** — As we have seen (p. 11), one kind of explanation consists in imagining some fact or connection of facts, or some machinery which, if it existed, would account for the phenomena to be explained. This we call an hypothesis. Hypotheses are of two kinds, stochastic and formulative.

The first of these is constantly used at every step in investigation, although it is seldom mentioned in books. When Mitscherlich discovered that Glauber's salt (p. 151) gave a definite pressure of water vapor, he at once formed the hypothesis, that is, supposition, that other hydrates would be found to do likewise. Experiments showed this supposition to be correct. The hypothesis was at once displaced by the fact. This sort of hypothesis predicts the probable existence of certain facts or connections of facts, hence, reviving a disused word, we call it a **stochastic hypothesis** (Gk. *στοχαστικός*, apt to divine the truth by conjecture). It professes to be composed entirely of verifiable facts and is subjected to verification as quickly as possible.

**Formulative Hypotheses.** — The formulative hypothesis is mainly a structure existing in the imagination. It may not be capable of existing anywhere else, because it may include items which are more or less in conflict with ordinary experience. But then, we use a formulative hypothesis for the purpose of having before our minds some sort of machinery that will help us to understand some aspect of the behavior of matter or energy, and we make few, if any, attempts to verify the hypothesis itself. Thus, the conception of light as consisting of corpuscles was such an hypothesis in its day. The imponderable-matter (note the contradiction) view of heat was another. The undulatory theory of light, which postulates a perfectly elastic ether, weightless, frictionless, and lacking every trace of impenetrability, is an hypothesis showing the same unverifiable elements. It is handled characteristically also, for we do not try by its means to learn more about ether, but more about light.

Such an hypothesis is like a scaffolding, constructed to enable us to examine or work upon a difficultly accessible part of a building, which we never for a moment think of as being a part of the building. It is a sort of formula. The algebraic formula represents magnitudes; the geometrical, directions and dimensions. The formula in physics, by the use of mathematical conventions, pictures, for example, some mode of behavior of matter. For so concrete a subject, however, the mathematical mode of expression is intensely abstract.

And so a representation in terms of mechanism, which is still a formula, is frequently resorted to. The hypothesis of the ether is therefore a formula consisting of imaginary machinery. Its object is simply to help us in organizing or formulating knowledge on a certain subject. Hence we name it a **formulative hypothesis**.

The kinetic molecular view was at first an hypothesis of this kind. It is only recently that we have been able to count the molecules of helium given off by radium (*q.v.*) and to see and to photograph the path of each molecule. These, and other observations, have now shown that molecules really exist, and behave as the hypothesis assumed they did. But the conception of molecules was no less useful before it had been verified than it was afterwards. Dalton, who first worked out a clear conception of the independent behavior of mixed gases (p. 111), used this as an hypothesis constantly in that work. Clear understanding of the separate existence of aqueous vapor in the air could be reached by him only by thinking of each material as being made up of independent molecules. Any other mode of conceiving the mixture that might readily occur to one would involve some adhesion or interference of the two substances. His recognition of the independent solubilities of mixed gases, in proportion to the partial pressures of each, would have been delayed or prevented altogether if, in studying the results of his experiments, he had not reached it by way of this hypothesis.

**Exercises.** — 1. What are the relative rates of diffusion of ammonia gas (density 17) and of sulphur dioxide (density 64)?

2. What are the speeds in meters per second of the molecules of ammonia and of sulphur dioxide at room temperature?

3. Give two ways of obtaining crystals of a substance.



## CHAPTER X

### SOLUTION

WE have frequently made use of the fact that certain substances form with others homogeneous systems which we call solutions. Sometimes this property is taken advantage of for separating materials, as in the case of the removal of sulphur from admixture with iron or ferrous sulphide (p. 15). In other cases we carry out the interaction of chemical substances, by first dissolving each in some liquid and then mixing the solutions. The liquid, commonly water, is used as a vehicle for one or more of the substances, and often takes no part in the chemical change. Thus some knowledge of the properties of solutions is absolutely necessary in order that we may employ them intelligently. In what follows, we shall give a preliminary account of some of the simpler facts about solution.

**General Properties of Solutions.**—A solid may be distributed through a liquid either by being simply **suspended** (p. 142) in the latter (**mixture**) or by being dissolved in it (**solution**). Similarly, a liquid may be suspended in droplets in another, like the fat in milk (**emulsion**), or it may be dissolved. It is usually easy to distinguish between the two cases, for a suspended substance *settles* or *separates* sooner or later (like the fats in milk — as cream) while a dissolved one shows *no such tendency*. The cases are exceptional where the subdivision of a suspended substance is so minute (**colloidal suspension**, *q.v.*) as to make its retention by filter paper impossible. If a liquid is opalescent or opaque, then we have a case of suspension. A solution is a clear, transparent, perfectly homogeneous liquid, in which the dissolved substance seems to have been dispersed so completely that the liquid cannot be distinguished by the eye from a pure substance.

There is no limit to the amount of dissipation which may thus be produced. A single fragment of potassium permanganate, for example, which gives a very deep purple solution in water, may be dissolved in a liter or even in twenty liters of water, and the purple tinge which it gives to the liquid will still be perfectly perceptible in every part of the larger volume. **The qualitative characteristics,**

therefore, of solution are absence of settling, homogeneity, and extremely minute subdivision of the dissolved substance.

**The Scope of the Word.** — The word is used for other systems than those containing a solid body dissolved in a liquid. Thus, liquids also may be dissolved in liquids, as alcohol in water. Again, if we warm ordinary water, bubbles of gas appear on the sides of the vessel before the water has approached the boiling-point. They are found to be gas derived from the air. Agitation of any gas with water results in the solution of a large or small quantity of the gas, and heating will usually drive the gas out again. It appears therefore that **solids, liquids, and gases can equally form solutions in liquids.**

The absorption of hydrogen by palladium (at all events after a certain point) and by iron takes place in accordance with the same laws as the solution of solids in liquids, and the results may be described therefore as true solutions. Liquids are in some cases absorbed by solids, and homogeneous mixtures of solids with solids are perfectly familiar. The sapphire is a solution of a small amount of a strongly colored substance, in a large amount of colorless aluminium oxide. It may therefore be stated that **solution of gases, liquids, and solids in solids** appears to be possible.

**Limits of Solubility.** — The next question which naturally occurs to us is as to whether the mingling of two substances in this manner has any limits. We find that the results of experiment in this direction may be divided into two classes. Some pairs, of liquids particularly, may be mixed in any proportions whatever. Alcohol and water, and glycerine and water are such pairs. On the other hand, at the ordinary laboratory temperature, we can scarcely take a fragment of marble  $\text{CaCO}_3$  so small that it will dissolve completely in 100 c.c. of pure water, for only 0.00013 g. dissolves. Under the same conditions any amount of potassium chlorate up to about 5 g. will completely disappear after vigorous stirring, while 90 g. of ordinary Epsom salts (hydrated magnesium sulphate), but not more, may be dissolved in about the same amount of water. In fact, most solids may be dissolved in a liquid only up to a certain limit, which with different solids may range from a scarcely perceptible up to a very large amount. No substance is absolutely insoluble. But for the sake of brevity we call marble, for example, **insoluble**, because in most connections it may be so considered.

Chemists have not yet succeeded in explaining these differences in solubility, which are often so surprising. Thus, guncotton (cellu-

lose nitrate) is soluble in a mixture of alcohol and ether, but not in these liquids separately. On the other hand, cellulose acetate, an allied substance, used in making bristles for brushes and artificial horsehair, is soluble in these liquids separately, but not in the mixture! Again, silver fluoride is extremely soluble in water, while the allied chloride, bromide, and iodide of silver are very insoluble (see Table, inside front cover). Conversely, calcium fluoride is very insoluble, but the chloride, bromide, and iodide are quite soluble.

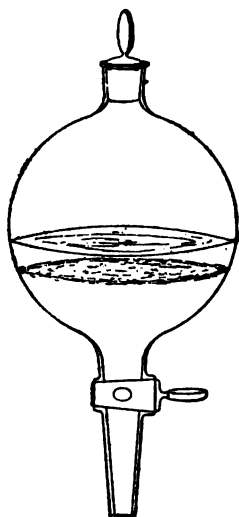


FIG. 74.

### **Recognition and Measurement of Solubility.**

— The only method of recognizing with certainty whether a solid is soluble in a liquid or not is to filter the mixture and evaporate a few drops of the filtrate on a clean watch-glass. For learning how much of the body is contained in a given solution, a weighed quantity of the solution is evaporated to dryness and the weight of the residue determined. When the dissolved substance is volatile, its presence is often shown by some chemical test (p. 89).

Ether and water is a case typical of the behavior of two liquids, each somewhat soluble in the other. After being shaken together, they seem to separate again completely into two layers (Fig. 74), with the ether uppermost. If, however, the water is withdrawn from beneath the ether, we find that, when heated, it gives off quantities of ether vapor which can be set on fire. Conversely, the addition of anhydrous cupric sulphate to a sample of the ether shows the presence of water in the latter, for the blue hydrated form of the substance is at once produced. In some common cases the maximum solubilities at room temperature are as follows:

SUBSTANCE.	VOL. IN 100 VOLS. Aq.	VOL. Aq. IN 100 VOLS.	GRAMS IN 100 g. Aq.	GRAMS Aq. IN 100 g.
Alcohol . . . . .	No limit	No limit	No limit	No limit
Ether . . . . .	8.11	2.93	5.97	3.98
Chloroform . . . . .	0.42	0.15	0.66	0.10
Carbon disulphide . . . . .	0.17	0.96	0.22	0.74

It must be stated explicitly that in going into *solution*, as we have used the term, a compound dissolves as a whole and, if the compound is pure (p. 6), any residue has the same chemical composition as the part which has dissolved. If the undissolved residue is a different substance, a chemical interaction with the solvent has occurred. If, on evaporation, a different substance remains, there has also been chemical action.

**Terminology.** — In order to describe the relations of the components of a solution, certain conceptions and corresponding technical expressions are required.

It is customary to speak of the substance which, like water in most cases, forms the bulk of the solution, as the **solvent**. To express the substance which is dissolved, the word **solute** is frequently used, and will be employed when we wish to avoid circumlocution.

The term "strength" is too indefinite for scientific purposes. It may imply activity, or power of resistance, or pungency (in an odor), or, as in the case of solutions, it may be a measure of quantity. The amount of the substance which has been dissolved by a given quantity of the solvent is therefore described as the **concentration** of the solution. A solution containing a small proportion of the dissolved body is called **dilute**; it has a small concentration. One which contains a larger amount is **more concentrated**. Very "strong" solutions are frequently spoken of simply as **concentrated solutions**. The *partial* removal of the solvent by evaporation is called **concentrating**, its total removal **evaporating to dryness**.

Finally, since there is a limit to the solubility of most substances, a solution is described as **saturated** when the solute has given as much material to the solvent as it can. This state is reached after prolonged agitation with *an excess* of the gas, of the liquid, or of the *finely powdered* solid, as the case may be (see pp. 192, 194). The larger the excess, the *sooner* saturation is attained, but the concentration is no greater. The maximum concentration attainable in this way is called the **solubility** of the substance in a given solvent. Note that a saturated solution need not also be a concentrated one. It will be very dilute, if the solute is but slightly soluble.

The distinction between solute and solvent is made merely for convenience. Theoretically, there is no distinction between the components of a solution.

**Units Used in Expressing Concentrations.** — The concentrations of solutions, saturated and otherwise, are sometimes ex-

pressed in physical, and sometimes in chemical, units of weight. When **physical units** are employed, as in the above table, we give the number of grams of the solute held in solution by one hundred grams (in the case of water 100 g. = 100 c.c.) of the solvent.

The **solubilities at 18° of 142 bases and salts** are given in a table, placed inside the front cover of this book.

When **chemical units** of weight are employed, two different plans are possible, and both are in use. Either the equivalent (p. 63) or the molecular weights may be taken as a basis of measurement. In the former case, the solutions are called **normal solutions**, and in the latter, for a reason which will appear later (Chap. XII), **molar solutions**.

A **normal solution** contains one gram-equivalent of the solute in one liter of solution (*not* in 1 l. of solvent). The word "equivalent" has been used hitherto only of elements, and this application of the expression involves an extension of its meaning. An **equivalent weight of a compound** is that amount of it which will interact with one equivalent of an element. Thus, a formula-weight of hydrochloric acid HCl (36.5 g.) is also an equivalent weight, for it contains 1 g. of hydrogen, and this amount of hydrogen is displaceable by one equivalent weight of a metal. A formula-weight of sulphuric acid H<sub>2</sub>SO<sub>4</sub> (98 g.), however, contains two equivalents of the compound, and a formula-weight of aluminium chloride AlCl<sub>3</sub> (133.5 g.) three equivalents. Hence normal solutions of these three substances contain respectively 36.5 g. of HCl,  $\frac{1}{2}$  of 98 g., or 49 g. of H<sub>2</sub>SO<sub>4</sub>, and  $\frac{1}{3}$  of 133.5 g., or 44.5 g. of AlCl<sub>3</sub> per liter of solution. The special property of normal solutions is, obviously, that equal volumes of two of them contain the exact proportions of the solutes which are required for complete interaction. Solutions of this kind are much used in quantitative analysis.

Solutions of different concentrations all prepared on the above basis are named as follows, and are often indicated by the abbreviations appended:

QUANTITY OF SOLUTE PER LITER.	NAME.	ABBREVIATIONS.
One hundredth of one gram-equivalent . . . . . }	Centi-normal	$\frac{N}{100}$ or .01 N
One tenth of one gram-equivalent . . . . . }	Deci-normal	$\frac{N}{10}$ or .1 N
One half of one gram-equivalent . . . . . }	Semi-normal	$\frac{N}{2}$ or .5 N
One gram-equivalent . . . . .	Normal	N
Two and a half gram-equivalents	Two and a half normal	2 $\frac{1}{2}$ N or 2.5 N

**A molar solution contains one mole (gram-molecular weight, see p. 183) of the solute in one liter of solution (not in 1 l. of solvent).** When molecular formulæ (see Chap. XII) are used, this means one gram-formula weight per liter. In the cases cited above, the molar solution contains 36.5 g. HCl, 98 g.  $\text{H}_2\text{SO}_4$ , and 133.5 g.  $\text{AlCl}_3$  per liter. As will be seen, the concentration of molar and normal solutions are necessarily identical when the radicals are univalent. Other concentrations are described as deci-molar ( $M/10$  or  $.1 M$ ), two and a half molar ( $2.5 M$ ), and so forth, on the same plan as before.

There is also a chemical unit of volume (see Chap. XII) which is the volume occupied by a mole (gram-molecular weight) of a gas (or dissolved substance) at  $0^\circ$  and 760 mm. pressure (gaseous or osmotic). This volume averages 22.4 liters, and is called the gram-molecular or molar volume (G.M.V.). The unit of concentration for many theoretical purposes is, therefore, that of one mole in 22.4 liters.

**Solution One of the Physical States of Aggregation of Matter.**— When a solid body dissolves in a liquid, the properties of the body undergo a very marked change, which to all appearance might be chemical. Yet, besides the ease with which the liquid may be removed by evaporation and the solid recovered unchanged, we note particularly that the concentration of a saturated solution cannot be expressed in terms of integral multiples of the atomic weights. If, therefore, the process were to be regarded as chemical, several important generalizations would have to be revised or discarded (*cf.* p. 61). We shall see also, in a later paragraph, that the quantity of a solid which a liquid may take up varies with the slightest change in temperature. Now we do not find the composition of chemical compounds so to vary. The solution of a solid may therefore be likened to a change in state, similar to the conversion of a liquid into a gas or a solid (*cf.* p. 49).

As there is danger of confusion arising, we may repeat that a compound is homogeneous and its composition is expressible in integral multiples of the chemical units of weight (atomic weights); a saturated solution is homogeneous but its concentration varies gradually with temperature so that integral multiples of the chemical units cannot be used to describe its composition; a mixture of two solids or an emulsion of two liquids, is neither homogeneous nor in any way definite in composition.

**Kinetic-Molecular View of the State of Solution.**— Accepting solution as a physical state of aggregation, we may now apply the same molecular conceptions to the explanation of the behavior of a substance in solution as to matter in the gaseous or liquid states. We

saw that a solid body, which is ordinarily condensed in a small space, can be disseminated by the use of a solvent through a very large one. The molecules of the solid become scattered, like those of a gas or vapor, through a much greater volume. We may regard the dissolved substance as being, practically, in a gaseous or *quasi-gaseous* condition. The molecules are torn apart from one another, their cohesion is overcome, and their freedom of motion is in a measure restored. It is true that they could not continue to occupy this large volume for a moment in the absence of the solvent. But we may bring this into relation with the case of a vapor by saying that a solid body, like common salt, can only evaporate (*i.e.*, dissolve) appreciably at the ordinary temperature, and occupy a large space, when that space is already filled with a suitable liquid. The latter acts as a vehicle for the particles of the solid. A volatile liquid, on the contrary, can dissolve in an *empty* space and fill it with its particles without any vehicle being required.



FIG. 75.

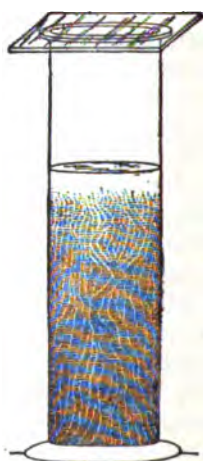


FIG. 76.

This conception of the *quasi-gaseous* condition of a dissolved substance would be simply fantastic if it did not lead us to a better understanding of the behavior of solutions. It does successfully explain many facts about solutions, such as diffusion, and saturation (see next section).

It is easy to show that, if we place a quantity of the pure solvent

(Fig. 75) above a concentrated solution of a substance, and then set the arrangement aside, the dissolved body slowly makes its way through the liquid (Fig. 76), obliterating the original plane of separation. Eventually the dissolved body scatters itself uniformly through the whole. In other words, the particles of the dissolved substance exhibit the property of **diffusion** in the same way as do those of gases.

When the diffusion of a *gas* is resisted by a suitable partition, we find pressure is exercised upon the walls of the vessel and upon the partition. It is possible to show that the particles of a *dissolved substance* induce a pressure of a very similar kind. This pressure is spoken of as **diffusion pressure**, and is proportional to the concentration of the solution. In other words, it depends upon the degree of crowding of the molecules of the dissolved substance.

**Kinetic-Molecular View of the Process of Solution.** — We may now apply the same ideas to the process of dissolving, with a view more especially to explaining why the process of dissolving ceases, in spite of the presence of excess of the solute, when a certain concentration has been reached. If some of the material dissolves, why not more?

Let us suppose that it is the dissolving of common salt in water (Fig. 77) which we wish to explain in detail. We believe that in the solid substance the molecules are closely packed together, while in the solution they are rather sparsely distributed. If there were no water over the salt, practically none of the particles of the latter would be able to leave the solid and enter the space above. Thus, the process of solution must consist in the loosening of the molecules on the surface and their passage into the liquid. By diffusion, the free molecules will gradually move away from the neighborhood of the surface of the solid and make room for others, and thus, if the system remains undisturbed, the liquid will eventually become a solution of uniform concentration. If a large enough amount of the solid has been provided, the ultimate condition will be that of a saturated solution with excess of the solid beneath. If we had proper means of measuring it, the tendency of the molecules to leave the

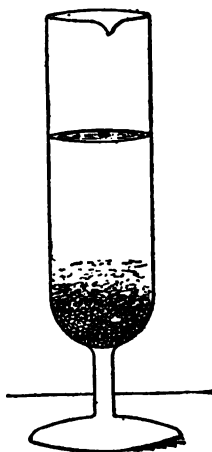


FIG. 77.



solid in the presence of a given liquid would give the effect of a kind of pressure. This is spoken of as **solution pressure**.

Now the molecules, after having entered the liquid, move in every direction, and consequently some of them will return to the solid and attach themselves to it. The frequency with which this will occur will be greater as the crowding of particles in the liquid increases, so that a stage will eventually be reached at which the number of molecules leaving the solid will be no greater than that landing upon it in a given time. If the whole of the liquid has meanwhile become equally charged with dissolved molecules, there will be no chance that the field of liquid immediately round the solid will lose them by diffusion, so that a condition of balance or equilibrium (p. 169) will have been established:  $\text{NaCl (solid)} \rightleftharpoons \text{NaCl (dissd)}$ . The presence of the particles in the liquid produces what we have called diffusion pressure; and *when the diffusion pressure, by the continual increase in the number of dissolved molecules, becomes equal to the solution pressure, increase in concentration of the solution ceases*. It is at this point that we speak of the solution as *being saturated* with respect to the particular substance dissolving. The analogy to vapor tension and vapor pressure (p. 168) is evident.

The foregoing explanation should be compared carefully with that given in the section on the molecular relations in liquids, and in that on equilibrium (pp. 168–170).

**Solution Pressure and Solution Suction.**—It should be noted that the term solution pressure really presents a one-sided view of the situation. When we place sulphur in carbon disulphide, it dissolves freely, and we should therefore say that sulphur has a high solution pressure. But when we put sulphur in water, hardly any dissolves, and we should then say that sulphur had almost no solution pressure. Clearly the tendency to dissolve is a *mutual property of the solvent and solute together*, and the term solution pressure is misleading because, when taken literally, it ascribes the result entirely to the solute. The ability of the solvent to take up the solute, which we might name the **solution suction** of the solvent, is at least equally important. It is not simply a question of how strongly the sulphur can throw off molecules, but also of how liberally the solvent is able to mix with these molecules. Water is not able to take up or to hold much sulphur, but carbon disulphide will extract or cohere with a large proportion of the very same sulphur. It is largely a question of some sort of physical affinity of the solvent for the solute. The term

solution pressure is, of course, understood by physical chemists to include this affinity or miscibility, but the words are far from conveying the idea to the student, and indeed seem explicitly to exclude it. Unfortunately, we have not yet been able to discover or invent any explanation of why some pairs of substances are so freely miscible, while other pairs are practically immiscible.

**Independent Solubility.** — Just as two gases, when mixed, are independent of one another (p. 111), and have severally the same pressure, solubility, and so forth, as they would possess if each alone occupied the same space, so it is with dissolved substances. In general, a volume of water, in which a small amount of some substance has been dissolved, will take up as much of a second substance as would an equal volume of pure water. Thus, water containing some sugar will dissolve as much sodium chloride as the same amount of pure water. In the kinetic-molecular point of view, the dissolved molecules of sugar have no connection with, or influence upon, the mechanism which determines the solubility of the salt, namely, the exchange of salt molecules between the suspended, dissolving crystals and the solution.

Naturally this principle of independent solubility does not hold with any degree of exactness when the concentration of the substance already present is great. If much sugar is present, then the solubility of salt in the mixture will depend on the miscibility of salt with sugar, as well as on its miscibility with water, and the total solubility may be very different from that in water. It fails also when the two solutes interact chemically, as will usually be the case, for example, when each is an acid, base, or salt (see Chap. XIX). The solubility is affected in an especial degree when the two substances have one radical in common, as when they are nitric acid and a nitrate, or two chlorides (see Ionic equilibrium).

**Conditions Affecting the Solubility of a Gas.** — The same conceptions may be used to explain any case of solution. Let us take that of oxygen conducted into a bottle which is partially filled with water (Fig. 78), no other gas being present in the space above the liquid. As the molecules of the gas impinge upon the liquid, some of them pass into it and dissolve. The particles which have thus gained access to the liquid move about in every direction and, as they become more and more numerous, a larger and larger number will escape from the surface and pass back into the gaseous condition.

At first, this reaction will be slight, but eventually, as the solution increases in concentration, it must become equal in rate to the process of solution itself. It is assumed that the supply of gas is maintained at a uniform pressure, and therefore uniform molecular concentration, during the whole process. Once more we shall have a state of balance or equilibrium, and the liquid will be *saturated*, this time with a gas: Oxygen (gas)  $\rightleftharpoons$  Oxygen (dissolved). It is found, as the hypothesis would lead us to expect, that the concentration of the saturated solution of any given gas is proportional to the pressure at which the gas is supplied, that is, to the molecular



FIG. 78.

concentration of the gas (Henry's law).

The solubilities of *different* gases, even when their pressures are equal, varies much. This is due, of course, to their differing physical affinities for (miscibilities with) the liquid. One volume of water will dissolve 1300 volumes of ammonia at 0° and 760 mm., while it will dissolve only about 0.02 volumes of hydrogen under the same conditions. In one volume of alcohol, at 0° and 760 mm., 17.9 volumes of hydrogen sulphide or 0.07 volumes of hydrogen may be dissolved. Henry's law describes the behavior of any one gas with exactness only when low gaseous pressures, or gases whose solubility is small, are in question. Great solubility must be due in part, probably, to chemical union between a part, at least, of the gas and the solvent, or to cohesive influences which the molecules of the dissolved gas exert upon each other. The law, and the kinetic-molecular explanation of the law, on the other hand, consider only an ideal behavior involving complete chemical and physical independence of the molecules.

When a mixture of two gases is in contact with the solvent, the molecular viewpoint enables us successfully to foretell what will happen. The quantity of each gas which can remain dissolved must depend simply upon the frequency with which *its own* molecules strike the liquid, and must be independent of the presence of the other gas. Hence the solubility of each gas is the same as if it were present alone at its own partial pressure (Dalton's law, p. 111). In other words, each gas has the same pressure, and therefore the same solubility, as it would possess if it alone occupied the *whole* space above the liquid.

Air dissolving in water is an illustration of this principle. It does not dissolve as a whole, but the oxygen and nitrogen dissolve each in proportion to its intrinsic solubility and partial pressure.

It is easy, by the use of this law, to form an approximate estimate of the proportion of oxygen to nitrogen in the dissolved gases. The air may be taken to be at 760 mm., and its composition by volume roughly  $1/5$  oxygen and  $4/5$  nitrogen. The separate solubilities of the gases at 760 mm. are, respectively, 4 and 2 volumes in 100 volumes of water. Their partial pressure being  $1/5$  and  $4/5$  of an atmosphere, the amounts actually dissolved will be  $4 \times 1/5 = 0.8$  and  $2 \times 4/5 = 1.6$  in 100 volumes of water. The ratio of free oxygen to nitrogen in the water will therefore be 1 : 2. Thus, if we expel the dissolved gases by boiling the water, we find that they contain 33 per cent oxygen by volume while air contains only 21 per cent.

This equilibrium,  $\text{Gas (gaseous)} \rightleftharpoons \text{Gas (dissd)}$ , can be reached, naturally, from the other direction, namely by starting with a solution of the gas and a space above the solution containing, at first, none of the gas. The gas leaves the solution until the rates of emission and return become equal. Hence, a gas may be entirely removed from solution by bubbling a foreign gas through the liquid. The bubbles furnish the space to receive the emitted gas, and have a large surface, so that the process goes on rapidly. The bubbles also escape, and carry with them the emitted gas, so that, in this case, there is no re-solution. This is a case of nullifying one of the two opposed tendencies (p. 170).

**Two Immiscible Solvents: Law of Partition.**—An interesting application of the same ideas may be made to a case which occurs very commonly in chemical work. If we shake up a small particle of iodine with water, we find that it dissolves slowly, giving eventually a saturated but very dilute solution. If now ether in sufficient quantity be shaken with the aqueous solution, the greater part of the iodine will find its way into the ether, and be contained in the brown layer which rises to the top. The process of removing a substance partially from solution in one solvent and securing it in another is called **extraction**. We find in such cases that neither solvent can entirely deprive the other of the whole of the dissolved substance, if the latter is soluble in both independently:  $I (\text{in Aq}) \rightleftharpoons I (\text{in ether})$ . The partition of the substance takes place in proportion to its solubility in each solvent. It is found that any amount of the **solute**, up to the maximum the system can contain, provided this does not involve too high a concentration in either solvent, **is divided so that the ratio of the concentrations in the two solvents is always the same (Law of partition)**. In the case of iodine divided between water and ether, this ratio is about 1 : 200.

The aqueous solution of potassium iodide has a very great power of dissolving iodine, and we find that in the presence of this salt the ether leaves a much larger share of the element in the lower layer. A part of the iodine combines to form KI<sub>3</sub>, however, so that this is not a case of simple solution, and the law of partition does not hold. The chemical equilibrium (see Chap. XV) between free and combined iodine in the aqueous layer has to be considered.

This principle is used in Parke's process (*q.v.*) for extracting silver from molten lead, by means of melted zinc as the second solvent. It is employed in separating interesting compounds from animal secretions and vegetable extracts, and in purifying such compounds. Nicotine from tobacco and cocaine from coca-leaves, are secured in this way.

***Influence of Temperature on Solubility.*** — The quantity of a substance which we can dissolve in a fixed amount of a given solvent depends very largely upon the temperature of both. Usually the solubility increases with rise in temperature. Measurements may be made by the method described before (p. 180), using *excess* of the finely powdered solute with different portions of the same solvent in vessels kept at different temperatures. The most useful way of representing the results is to plot them graphically. The diagram (Fig. 79) shows the curves for a few familiar substances. The ordinates represent the number of grams of the anhydrous compound which is held in solution by 100 g. of water in each case. The abscissæ represent the temperatures. The concentration for any temperature can be read off at once. Thus 100 g. of water holds 13 g. of potassium nitrate in solution at 0° and 150 g. at 73°. The increase in solubility is here enormous. On the other hand, the same quantity of water will hold 35.6 g. of sodium chloride in solution at 0° and 39 g. at 100°. The difference is shown at once when we examine the curves and observe that the line representing the solubility of sodium chloride scarcely rises at all between 0° and 100°, while that of potassium nitrate is extremely steep.

Cases in which the solubility decreases with rise in temperature are less common. The solubility of slaked lime (calcium hydroxide Ca(OH)<sub>2</sub>, used to make limewater) is 0.175 g. at 20° and 0.0789, or less than half as great, at 100°. Anhydrous sodium sulphate Na<sub>2</sub>SO<sub>4</sub> (Fig. 80, p. 193) is another illustration. When triethylamine, an organic base, N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, liquid at ordinary temperatures, is added to cold water until no more will dissolve, the solution, which is perfectly clear and transparent, on being warmed with the hand at once be-

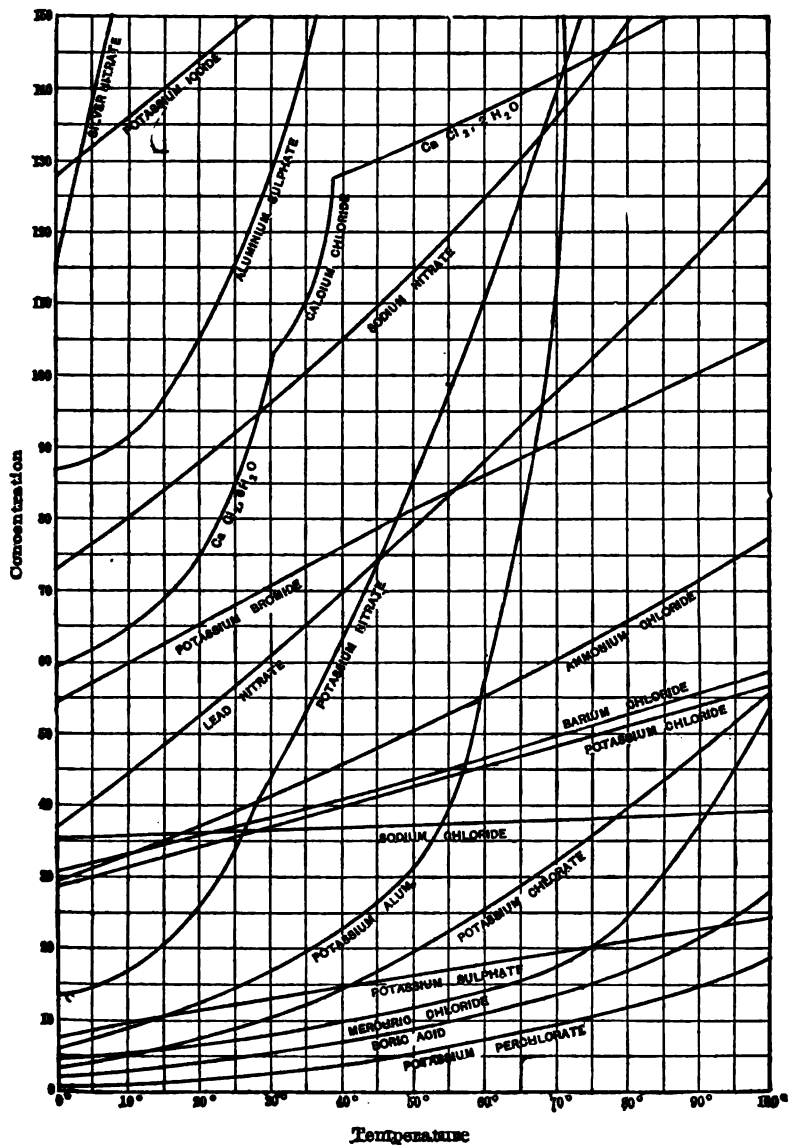


FIG. 79.

comes clouded from the separation of the two liquids. A comparatively slight elevation in temperature causes a separation into two distinct layers.

**Phases.** — We can frequently abbreviate our statements by using two words of broad significance, one of which has already been employed. A set of materials in, or tending towards, a condition of equilibrium is called a **system**. The discrete parts of an inhomogeneous system are called its **phases**. Thus, a liquid with its vapor forms a system with a liquid phase and a vapor phase. A saturated solution is a system with three phases, the undissolved excess of the solute (solid phase), the solution, and the vapor.

**Equilibrium in a Saturated Solution.** — Once a solution has become saturated, the undissolved material remains thereafter unchanged *in amount*, no matter how long the materials are left in contact. In technical terms, the quantity of each phase has no influence on the concentration of any of them. A *greater* excess of the solute forces no more matter into solution than does a small excess.

It should be clearly understood, however, that the kinetic theory requires us to assume that an exchange of molecules (p. 186) is still going on between the solid and the solution. That this conception is correct may be shown in various ways. Thus, if a crystal, the edges or corners of which have been broken, is suspended in a saturated solution of the same substance, it neither increases nor diminishes in weight. Yet we find that the imperfections are removed, and that this takes place by the solution of a portion of the substance from the perfect surfaces and its deposition upon the imperfect ones.

**Supersaturated Solutions.** — Another very striking proof of this may be obtained by saturating water with ordinary Glauber's salt (hydrated sodium sulphate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) at a temperature somewhat above the ordinary, say  $30^\circ$ , at which temperature 100 c.c. of water hold in solution 40 g. of  $\text{Na}_2\text{SO}_4$  (Fig. 80). The excess of the solid is carefully and completely separated from the liquid, and the latter is allowed to cool, say to  $15^\circ$  in a flask loosely stoppered with cotton. The solution now contains (Fig. 80) a much larger amount of sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) than at its present temperature it could acquire from contact with Glauber's salt (13 g. at  $15^\circ$ ). Yet in the absence of a crystal, with which the above described exchange could take place, no deposition of the dissolved substance begins. The

solution may be kept indefinitely without alteration. The introduction, however, of the minutest fragment of the decahydrate at once starts the exchange, and this is necessarily very much to the

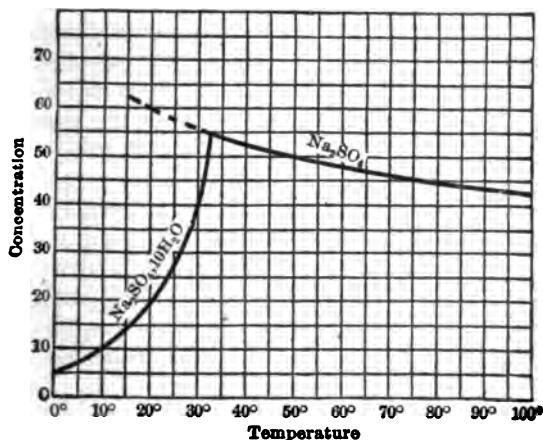


FIG. 80.

disadvantage of the solution and the advantage of the crystal:  $\text{Na}_2\text{SO}_4 \text{ (dissolved)} + 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \text{ (solid)}$ . The latter therefore forms the center of a radiating mass of blade-like processes, which sprout with astonishing rapidity through the liquid (Fig. 81).

Usually the cooling of a concentrated solution leads to the almost immediate appearance of crystals spontaneously, and the substance is deposited gradually as the temperature falls. But solutions of a number of common substances, such as sodium thiosulphate (photographer's "hypo") and sodium chlorate, behave like that of sodium sulphate. They are said to have a tendency to give **supersaturated solutions**. In general, crystallization can be started only by introduction of a specimen of the same substance, or at all events of one isomorphous (*q.v.*) with it. The smallest particle of the right material floating in the air, if it gains accidental admission, will bring about the result. This shows the importance of the interchange of molecules of which we have spoken for establishing equilibrium.

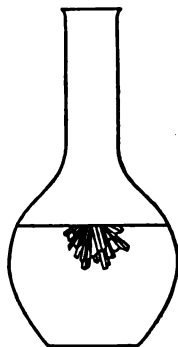


FIG. 81.



**Metastable Condition.**—The above phenomenon is not an isolated or exceptional one in physical science. It is commonly the case that, when the conditions for some physical change have been reached, the beginning of the physical change is delayed or entirely fails. The system is then said to be in a **metastable** condition. Unstable it is not. Yet it is not in the state of greatest stability, for the element of equilibrium is lacking. Thus, pure water may easily be cooled three or four degrees below  $0^{\circ}$  without the appearance of any ice. Agitation, however, in this case, results in the appearance of ice sooner or later. Addition of a fragment of ice results in immediate crystallization (freezing). In like manner water may be heated to a temperature above  $100^{\circ}$  without boiling. Drops of water, suspended in some oil of almost the same specific gravity, may even be raised to  $175^{\circ}$  before the water turns into steam. This is because there is no water vapor (but only oil) in contact with the water. Similarly, air which is saturated with moisture, if it contains no dust, may be cooled without the appearance of fog.

Phenomena of supersaturation, of a temporary kind at least, are extremely common in chemistry. Almost every delayed precipitation is a case of it. Barium sulphate, for example, is always slow in appearing in dilute solutions. So is sulphur, set free from dilute sodium thiosulphate solution by the action of an acid. In the latter case, instant reneutralization with a base does not prevent the ultimate appearance of the sulphur, showing that the cause does not lie in slow interaction of the salt with the acid.

**Definition of a Saturated Solution: A Warning.**—To avoid a common **misconception**, it must be noted that a saturated solution must *not* be defined as one containing all of the solute that it *can hold*. A supersaturated solution holds more. The **saturated solution** is one which contains all of the dissolved solute that it can acquire from the undissolved solute. Better still, it is **that solution which, when placed with excess of the solute, is found to be in equilibrium.**

It must be clearly understood that solution is *not* a process of filling the pores of the liquid. If that were true, approximately equal weights of all substances would find accommodation in equal volumes of water. The fact is that, for example, 100 c.c. of water can dissolve 195 g. of silver fluoride, but only 0.00000035 g. of silver iodide, although the space available in the solvent (if there is any free space) is the same in both cases.

The same conclusion is reached when we consider that two *forms* of the *same compound* have *different* solubilities. Thus, at  $20^{\circ}$ ,

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  can give about 18 g. of  $\text{Na}_2\text{SO}_4$  to 100 c.c. of water (Fig. 80). But *anhydrous* sodium sulphate  $\text{Na}_2\text{SO}_4$  at  $20^\circ$  gives 59 g. to the same amount of water (read up to dotted line, Fig. 80).

**Saturation.** — When we have shaken a solid for a sufficient length of time with a given amount of a liquid, we obtain a solution which is saturated with respect to that substance. Having called this a *saturated solution*, we are inclined to extract from the term a meaning different from that which it was really intended to convey. We are in danger of thinking that the solution itself is in some way peculiar — that, for instance, it contains all of the solid which it is capable of holding. This would be an entire misconception. If we desire to make a solution of sodium sulphate  $\text{Na}_2\text{SO}_4$ , for example, we may present this substance to the water either in the form of Glauber's salt  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  or of anhydrous sodium sulphate. Now the anhydrous and the hydrated forms of a substance always behave like entirely different substances. This hydrate cannot give more than 5 parts of sodium sulphate  $\text{Na}_2\text{SO}_4$  to 100 parts of water at  $0^\circ$ . When the anhydrous compound is used, many times this amount (Fig. 80) is dissolved at the same temperature:  $\text{Na}_2\text{SO}_4$  (solid)  $\rightleftharpoons$   $\text{Na}_2\text{SO}_4$  (dissd). The solution pressures of the two forms are entirely different. The phrase, "a saturated solution of sodium sulphate," is therefore devoid of definite meaning. We must describe the liquid as a solution saturated by anhydrous, or by hydrated sodium sulphate as the case may be.

Being different substances, the hydrated and anhydrous forms of a compound must be investigated separately as to their solubility at various temperatures. The results must give different curves, as for distinct substances.

Before referring to the curves of the two sodium sulphates, it must be remarked that hydrates decompose into the anhydrous, or some less hydrated form at a definite temperature. We cannot therefore continue the observation of the solubility of the substance beyond the temperature at which it ceases to exist. Thus the solubility curve of a hydrate comes to an abrupt termination at the decomposition, or, as it is usually called, the transition point.\* Now the decahydrate of sodium sulphate melts and decomposes at  $32.4^\circ$ , so that its solubilities can be measured only from about  $0^\circ$  to  $32.4^\circ$ . The solubility of the anhydrous form, however, can be investigated up to  $100^\circ$ , or beyond it, if necessary. Not only so, but measurements can be carried out below  $32.4^\circ$ . There is time to saturate the

\* These statements refer to equilibrium conditions. In practice, by rapid work, measurement of the solubilities of hydrates can usually be made *above* the melting (transition) point also.

solution with the anhydrous body, and decant the liquid for analysis, before the hydrate begins to crystallize out.

The solubility of the decahydrate (Fig. 80) rises rapidly between  $0^{\circ}$  and  $32.4^{\circ}$  from 5 to 55 parts in 100. The solubility of the anhydrous sodium sulphate decreases steadily from more than 55 parts below  $32.4^{\circ}$  to 42.5 parts at  $100^{\circ}$ . The character of the two bodies, in the matter of solubility, is therefore entirely different. The solutions themselves, as has been said already, are identical in every way, when they have the same concentration, whether they have been made from the one substance or the other.

Let us return now to the proper use of the term "saturated solution." We might say, correctly, that at  $20^{\circ}$  a solution made from hydrated sodium sulphate and containing 19.4 parts of sodium sulphate in 100 of water was saturated. This would *not*, however, be the maximum quantity which the same amount of water could hold, for, with the help of the anhydrous compound, we could add an amount equivalent to prolonging the ordinate at  $20^{\circ}$  until it intersected the curve of anhydrous sodium sulphate somewhere about the value 60. Nor can we be sure that even then the water would contain all the sodium sulphate which it *could hold*. It is conceivable that, by presenting the substance in some still other form, even greater solubility might be observed.

A saturated solution, if we fix our minds upon it simply as a solution, is not different from any other solution. There is no feature in the properties of such a solution, *qua* solution, which distinguishes it in the least from one containing slightly less or one containing slightly more of the dissolved substance. In contact with a crystal of the substance used to produce the saturation, however, the saturated solution is found to be in equilibrium, while the unsaturated solution takes up more of the substance, and the supersaturated solution at once deposits the amount which it contains in excess of the saturated solution. The words unsaturated, saturated, and supersaturated convey, therefore, no meaning unless we add that the solution is so towards some specific form of material. These are qualities of the system including the undissolved body, and not of the solution by itself.

The fact that the hydrated and anhydrous sodium sulphates give saturated solutions of the same concentration at  $32.4^{\circ}$ , so that the curves intersect at this point, is a very significant one. This is the temperature at which the former substance turns into the latter. At transition points like this the values of solubility, vapor pressure, and some other properties, are always the same for both forms (see Freezing-points of solutions).

***The Solute Modifies the Physical Properties of the Solvent.***—These alterations in the values of the physical properties of the solvent are divisible into two classes. In one of these classes, equal numbers of dissolved molecules of *different* substances, dissolved in equal quantities of the solvent, produce the same amount of change in the properties affected. The change is proportional to the molecular concentration of the dissolved body, when this concentration is

**small.** This effect appears, therefore, to be largely due to mechanical causes, since it depends simply upon the number of foreign molecules, without reference to the substance composing them. Of this nature are the lowering in the vapor tension of the liquid, the raising of its boiling-point, the lowering of the freezing-point of the liquid (see below), and the value of the osmotic pressure (see Chap. XVII).

In the other class, the extent of the effect varies in amount with the nature of the substance dissolved, even when equal numbers of molecules are used. This sort of modification in the properties is specific for each pair of substances (solvent and solute). The change in total volume occurring during solution, and the heat of solution (see below) belong to this class.

**The Vapor Tensions of Solutions.** — A solute, which is itself non-volatile, tends to diminish the vapor tension of the solution. It hinders the emission of the vapor. Thus if, instead of water, we introduce aqueous solutions of differing concentrations of the same substance successively into the barometric vacuum (Fig. 53, p. 145), we find that the **vapor pressures** of the solutions are less than that of water at the same temperature. The *diminution* in the fall of the mercury column, which measures the **lowering in vapor pressure**, is **proportional to the concentration of each solution**. The limit is reached with the saturated solution, although, if this is rather concentrated, the proportionality does not hold strictly down to that point (see Chap. XVII). For example, at 20°, water has the vapor pressure 17.4 mm. while a saturated solution of common salt (34.3 : 100 Aq) shows only 13.9 mm. — a lowering in the vapor pressure of the solvent by 3.5 mm.

If the substance is very soluble, and the solution highly concentrated, the lowering in the vapor tension will be considerable. In fact, the solution may give a vapor pressure of water less than that commonly present in the atmosphere. Such a solution, placed in an open vessel, will not evaporate. On the contrary, vapor from the air will enter it, and it will increase in bulk. For this reason, crystals of very soluble substances are usually moist and, when exposed to the air, acquire water from the latter and dissolve in this water. This behavior is called **deliquescence**, and is exhibited, for example, by the hydrate of calcium chloride  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , which is consequently used for drying gases. Magnesium chloride  $\text{MgCl}_2$ , present as an impurity in common salt, causes the latter to become moist in damp weather.

The principle involved will become clear if we imagine two vessels, one containing pure water and one an aqueous solution, to be placed

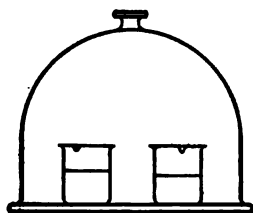


FIG. 82.

on a glass plate and covered by a bell jar (Fig. 82). Each liquid exchanges water molecules with the moist air in the jar, but the solution gives off water more feebly than does the pure water. The result is that the latter can produce a pressure of water vapor higher than that which would be in equilibrium with the solution. The solution, therefore, receives continuously more molecules than it emits, and increases in volume. The pure water thus gradually passes through the vapor state into the solution until it is all gone. If sufficient water was present, the process would go on until the solution became infinitely dilute.

One of the oddities of chemical literature is the fact that most authors discuss efflorescence (p. 151) and deliquescence in the same paragraph, if not in the same sentence. Since these two topics are entirely unrelated, and belong indeed to different chapters, this inappropriate juxtaposition is somewhat confusing.

**Elevation in the Boiling-Point of a Solution.**—A solute lowers the vapor pressure of a solvent, not only at room temperature, but at all temperatures. Thus, at  $100^\circ$ , a 7.5 per cent solution of potassium chloride shows a vapor pressure of only 734.1 mm., while that of water is 760 mm. The lowering is 25.9 mm. Hence, the solution has to be raised to a higher temperature ( $100.96^\circ$ ) before it boils. This is almost exactly  $0.037^\circ$  per 1 mm., which is the value for pure water (p. 145).

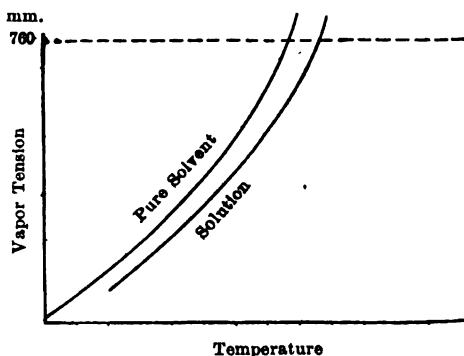


FIG. 83.

This conclusion may also be reached graphically (Fig. 83). The ordinates represent the vapor tensions corresponding to the temperatures shown by the abscissae. They increase in length with rise in temperature. The horizontal dotted line shows the vapor tension of 760 mm. at which any liquid will boil. The

boiling-point of the solvent is therefore the temperature at which its curve intersects this line. Since the vapor tensions of the solution are all below those of the solvent, its curve lies below that for the solvent, but ascends along with the latter. Hence, it also cuts the 760 mm. line, but at a point *beyond* the boiling-point of the pure solvent. Since, for short lengths, the curves are very nearly straight lines, the distances from boiling-point to boiling-point are very nearly proportional to the vertical distances between the curves. That is to say, the **elevations in the boiling-point are proportional to the depressions in the vapor tension, and therefore to the concentration of the different solutions of any one substance.**

When different substances in the same solvent are compared, equal molecular concentrations of the solute give equal elevations in the boiling-point. Thus, 1 gram-molecular weight of sugar (342 g.), or of glycerine (92 g.), dissolved in 1000 cc. of water, will elevate the boiling-point from 100° to 100.52° (for exceptions, see Chap. XVII). When the effects of the same solute in different solvents are compared, the scale of the elevation alone is different.

The same effect may be observed in isomorphous mixtures of solid bodies, which chemists consider to be solid solutions. Thus the vapor tension of water in the alums is greater than the average vapor pressure of water in the air, and hence they lose their water of hydration spontaneously (*cf.* p. 152). But if mixed crystals of two alums, say ordinary alum  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$  and iron alum  $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$  are prepared, they keep perfectly. The vapor tension of the water in each has been lowered by the influence of the other alum dissolved in it. Similarly, calcium formate  $Ca(CHO_2)_2 \cdot 4H_2O$  effloresces (p. 151), but loses this tendency when crystallized with some of the isomorphous barium or strontium salt.

**Freezing-Points of Solutions: Freezing Mixtures.** — Every pure liquid has a definite temperature at which it freezes. Thus, pure water freezes at 0° and benzene at 5.5°. The freezing of a dilute solution consists, usually, in the crystallization of some of the *pure solvent* only. The presence of a foreign, dissolved body, tends to prevent this freezing, and so solutions can be frozen only at temperatures below the freezing-point of the pure solvent. Thus, sea-water is harder to freeze than fresh water. Also, the ice formed in salt water is free from salt. **The freezing-points of solutions of the same substance are found to be depressed below that of the solvent in proportion to the concentration of the solute\*** (see Chap. XVII). This may be shown graphically (Fig. 84). The ordinates represent vapor tensions corresponding to the temperatures shown by the abscissæ. The rate at which the former rise is greater for ice than for water,

\* Only when the solid which separates consists of the pure solvent, and the solute does not enter into it, does this law represent the facts.

hence the ice curve is steeper. At  $0^\circ$ , ice and water can coexist permanently (p. 144). By measurement, they have the same vapor tension (4.6 mm.) at this point. Theoretically, if they had not, they could not coexist indefinitely, for the one with the greater vapor

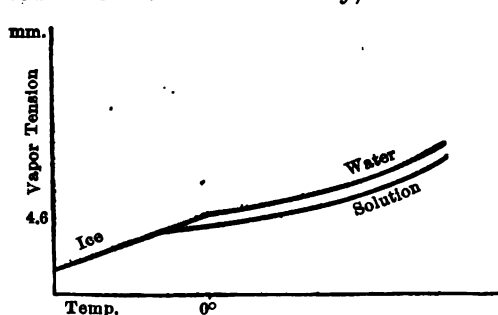


FIG. 84.

mm. and therefore behind  $0^\circ$ . In other words, ice and the solution cannot have equal vapor tensions, and therefore coexist indefinitely, except at some temperature below  $0^\circ$ . But the temperature at which ice can exist indefinitely in a solution is the freezing-point. Hence, freezing-points of solutions are always lower than those of the pure solvents.

By measuring the vapor tensions of the solution at several temperatures, in order to see how far the curve for the solution is below that of water, and then producing the curve for the solution backwards, the intersection with the ice curve, and therefore the freezing-point, may be obtained graphically. Direct measurement always confirms the result.

Since the ice curve is, for a short distance, almost a straight line, it follows that the depressions of the freezing-point are proportional to those of the vapor tension, and these in turn are proportional to the concentrations. From this relation we get the statement with which this section opened. Thus, solutions of sugar containing 11.4, 22.8, and 34.2 g. of sugar to 100 g. of water freeze at  $-0.62^\circ$ ,  $-1.23^\circ$ , and  $-1.85^\circ$ , respectively. Numerically, in the case of water, a lowering of the vapor pressure by  $\frac{1}{100}$  of its amount at each temperature sets the freezing-point back  $1.05^\circ$ .

This fact likewise explains why salt, thrown on ice, causes the latter to melt. A saturated solution of salt does not freeze until cooled to  $-21^\circ$  ( $-6^\circ$  F.), and it then gives a mixture of pure ice and pure salt crystals, known as a **cryohydrate**. Hence, ice and salt can

tension would evaporate, and its vapor would condense on the other until one of them alone remained.

Now the vapor tension of a solution is, at all temperatures, lower (Fig. 84) than that of water. Hence, for a solution, the curve must cut the ice curve below 4.6

not permanently exist together *above*  $-21^{\circ}$ , their cryohydratic point. Below  $-6^{\circ}$  F., salt will no longer melt ice because the solid mixture can exist below that temperature. A mixture of ice and salt, giving a temperature of  $-6^{\circ}$  F., is called a **freezing mixture**, and is used in freezing ice cream and ices. Substances more soluble than common salt, such as calcium chloride, give, with ice, freezing mixtures of lower temperature (see end of section on Heat of solution, p. 203).

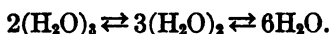
**Densities of Solutions.** — The density of a solution is usually greater, though often less, than that of water and, in each case, varies with the concentration. For commercial purposes, the concentration of a solution is commonly defined by the density (or specific gravity). Thus, we purchase ammonium hydroxide solution of "0.88 sp. gr.," meaning 35 per cent of ammonia, or sulphuric acid of "1.84 sp. gr.," meaning 94.8 per cent of the acid.

The commonly greater density of a solution is utilized in making solutions in chemical factories. Shaking several tons of the mixture is out of the question, and stirring costs money. If the solid is placed in the bottom of the tank, under water, a saturated solution is formed in the lowest layer of the water, and passage of the dissolving substance into the upper layers, by diffusion, would take months or years. Hence most of the solid would remain undissolved (Fig. 76, p. 184). But when the solid is placed on a *shelf*, near the surface of the water, the solution, being more dense, sinks through the water, fresh water rises to the shelf, and a circulation is started. This results in the dissolving of the whole material in a surprisingly short time, with no expenditure of labor whatever.

**Changes in Volume upon Solution.** — The erratic and, at present, unexplained changes in volume which occur when a substance is dissolved, seem to indicate that the process is less simple than we have thus far admitted, and that chemical changes occur during the process. Thus, when 250 g. of common salt are dissolved in 1 liter of water (= 1000 c.c. = 1000 g.), which gives a 20 per cent solution, the volume of the solution is only 1086 c.c. Since the 250 g. of salt occupied 116 c.c. before being dissolved, a *shrinkage* of 1116–1086, or 30 c.c., accompanied the process of solution. On the other hand, 214 g. of ammonium chloride (volume 142.5 c.c.) and 843.5 c.c. of water have a total volume of 986 c.c., but when dissolved give 1000 c.c. of solution. Here there is an expansion of 14 c.c. Table sugar, however, dissolves in water with almost no change in volume.



**Is Solution a Physical or a Chemical Change?** — These phenomena are, in part, accounted for by the fact that water is not a single substance, but a mixture. It is largely composed of dihydrol ( $\text{H}_2\text{O}$ )<sub>2</sub>, with much trihydrol ( $\text{H}_2\text{O}$ )<sub>3</sub> near to 0° and increasing quantities of monohydrol  $\text{H}_2\text{O}$  at higher temperatures. When *any* substance is dissolved in considerable amount in water, the equilibrium amongst these three kinds of molecules is disturbed, and their proportions change:



Now, equal weights of these three kinds of water occupy different volumes, and hence solution is accompanied by changes in the volume of the *water*. The same condition in water explains the point of maximum density (4°). The change from ( $\text{H}_2\text{O}$ )<sub>3</sub> to ( $\text{H}_2\text{O}$ )<sub>2</sub>, which proceeds as the temperature rises from 0° to 4°, is accompanied by a *shrinkage*, because dihydrol has the higher specific gravity. Beyond 4°, the usual expansion with rising temperature prevails.

There is also evidence that many dissolved bodies form unstable compounds with water, although we have not as yet definite information about these compounds.

Dissolving in water is, therefore, partly a chemical and only partly a physical process — a part of the water is always affected, and a part or all of the solute may go into combination.

**Heat of Solution.** — As in other changes of state of aggregation, so in the process of solution, heat is usually liberated or absorbed. That is, the solution is either warmer or colder than the original materials. This is known as **heat of solution**. Thus, one gram-formula-weight of sulphuric acid (98 g.), in dissolving in a large volume of water, liberates 39,170 calories, and one gram-formula-weight of ammonium chloride (53.5 g.), in dissolving, *absorbs* 3880 calories.

The sources or destiny of the heat given out or absorbed have not been studied in such a way that definite statements can be made about the theory of the subject. There are many factors which would have to be considered. For example, the body, if a solid, goes into an essentially liquid condition, and its heat of fusion is always negative. A part of the water always undergoes chemical change (p. 202). The solute also frequently combines with a part of the water, or is ionized (*q.v.*), and the change in volume of the mixture, as a physical phenomenon, would alone entail a heat-change. Hence this heat effect is partly chemical and partly physical in origin.

The first water used always causes a greater heat change than the addition of succeeding equal amounts. Heats of solution are measured for the solution of one formula-weight of the substance in unlimited water. The values in calories for some common substances are as follows:

$\text{H}_2\text{SO}_4$ , Aq = +39,170	$\text{NaCl}$ , Aq = -1180
$\text{HCl}$ , Aq = +17,400	$\text{NH}_4\text{Cl}$ , Aq = -3880
$\text{KOH}$ , Aq = +12,500	$\text{KCl}$ , Aq = -4440
$\text{NaOH}$ , Aq = +9780	$\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$ , Aq = -16,160
$\text{Na}_2\text{CO}_3$ , Aq = +5640	$\text{Na}_2\text{SO}_4$ , Aq = +460
$\text{CaCl}_2$ , Aq = +3258	$\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$ , Aq = -18,760

When a substance comes out of solution, the heat effect is equal, and of opposite sign to that occurring when the same substance goes into solution. Hence, since the decahydrate of sodium sulphate absorbs heat in dissolving, a considerable development of heat is noticed when it suddenly crystallizes from a supersaturated solution. Some ether in a tube immersed in the solution may be boiled by this heat and its vapor set on fire to make the fact evident at a distance. An important relation between heat of solution and solubility will be discussed under van't Hoff's law of mobile equilibrium (*q.v.*).

The melting of ice by contact with salt is sometimes explained as being due to the heat given out when the salt dissolves. The above table shows, however, that heat is absorbed — not given out — when salt dissolves. The fact is that any substance, provided it is soluble in water, when added to ice, will give a mixture with a temperature below  $0^\circ$ . Whether the substance is sulphuric acid, which gives out heat, or ammonium chloride, which absorbs it, makes no difference in the result. The solubility, in terms of the number of molecules that can be dissolved in a given amount of water, alone determines the extent of the depression in temperature (below  $0^\circ$ ) which is produced. The temperature falls because of the heat absorbed in melting the ice (ht. of fusion 79 cal. per 1 g.), and, in spite of the warmth of surrounding bodies, the temperature thereafter remains at the low value (so long as the ice holds out), because that is the temperature at which alone ice and the solution can coexist (p. 200).

**Definition of a Solution.** — We are now able to make a brief statement which shall distinguish solutions from mixtures on the one hand and from chemical compounds on the other. **Solutions are homogeneous mixtures of two or more substances which are separa-**

ble into their components by altering the state of one of the substances (*e.g.*, by freezing or boiling out one component), and whose properties vary continuously with the proportions of the components between certain limits.

**Application in Chemical Work.** — The theory of this subject has been given on account of its intensely practical interest, and it should be kept in mind in all ordinary chemical operations. It will afford an explanation of many things which might otherwise be attributed to the wrong cause, or might remain entirely without explanation. For example, why is the action of a metal upon an acid so slow? We must remember that an acid diluted with water is being used, and only one molecule out of every dozen or hundred is a molecule of the acid. So that the access of the latter to the metal is restricted at first, and becomes more and more so as the molecules of the acid in the immediate vicinity of the metal undergo chemical change.\* On the other hand, the metal, especially if it be in the form of sticks obtained by casting, presents one of the elements in the action in a most compact form. The only parts which are accessible to the acid are those upon the surface and, the metal not being appreciably soluble in water, the molecules can only pass off and expose a fresh layer very slowly. It is no wonder that many chemical actions occupy a considerable time. The wonder is that they should take place as rapidly as they do. Their speed would seem to point to a most intense chemical activity, even in the seemingly feebler instances. Various artifices are habitually employed for facilitating chemical action. Thus, the metal may be reduced to a leafy form by pouring the molten substance into cold water. Naturally, with metals, the maximum surface and the most rapid chemical action are obtained by using a fine powder.

The most speedy interaction of all, other things being equal, must be attainable by dissolving all the interacting substances in water. Under these circumstances all the molecules of each substance must simultaneously have many molecules of the other within easy reach of them.

\* In spite of the continuous exhaustion of the acid, there is often a steady increase in the rate at which a dilute acid interacts with a metal. This is due, at first, to the dirt on the surface of the metal which temporarily obstructs the action and, later, to the rising temperature of the interacting bodies. In the action of metals, like that of zinc on an acid (p. 119), impurities in the metal remain on the surface as the metal is eaten away and act as contact agents, stimulating the reaction.

**Exercises.** — 1. Give other examples of limited solubility in various solvents (p. 179).

2. If you were not permitted to evaporate sea-water to dryness, how should you show that it was a solution and not a pure substance?

3. Reexpress Henry's law (p. 188) in terms of the volume of gas dissolved at different pressures.

4. If hydrogen sulphide is diluted to ten times its volume with hydrogen, what volume of it, estimated as pure gas, will be dissolved by 20 volumes of alcohol at  $0^{\circ}$  and 760 mm. (p. 188)?

5. If the dissolved air, after being removed from water by boiling, were to be shaken with water once more, in what proportions by volume would the gases now dissolve (p. 189)?

6. Read from the curves (p. 191) the solubilities of potassium nitrate at  $15^{\circ}$ , of potassium chloride at  $30^{\circ}$ , of potassium chlorate at  $45^{\circ}$ . What are the relative rates at which the solubilities of these salts increase with rise in temperature?

7. Express the concentrations of solutions of ammonium chloride, saturated at  $0^{\circ}$  (sp. gr. 1.076), and of potassium sulphate  $K_2SO_4$ , saturated at  $10^{\circ}$  (sp. gr. 1.083), in terms of a normal solution (p. 182).

8. Express the concentration of a five per cent aqueous solution of phosphoric acid (sp. gr. 1.027), in terms of a normal and a molar solution, respectively.

9. Name the phases (p. 192) in a system consisting of oxygen and its aqueous solution, (a) above  $0^{\circ}$ , (b) below  $0^{\circ}$ .

10. When a solution of a very soluble substance, like zinc chloride, is evaporated to dryness on a water bath, why is the escape of the last portions of the solvent so much slower than is that of the first?

11. At what level in a tank of water should you introduce ammonia gas, in order, with the least effort, to saturate the water (p. 201)?

12. Give one reason why a gas, at constant pressure, should become less soluble as the temperature rises.

## CHAPTER XI

### HYDROGEN CHLORIDE AND CHLORINE

WE have had occasion several times to mention common salt, or sodium chloride NaCl. This is one of the most familiar chemical substances. Large quantities of it are used in the household, in cooking and in making freezing mixtures. Still larger amounts are consumed in manufacturing washing soda, caustic soda, and soap, for all of which it furnishes the necessary sodium. It is used also in preserving fish and other foods. It supplies the chlorine used in bleaching and in the sterilization of city waters. We shall consider it first as a means of making other compounds of chlorine.

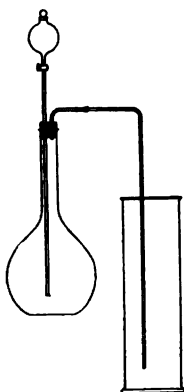
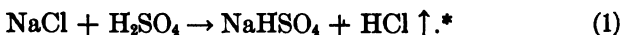


FIG. 85.

**Preparation of Hydrogen Chloride HCl from Salt.**—When some concentrated sulphuric acid is poured upon sodium chloride, a vigorous effervescence is noticed. This shows that bubbles of a gas are forming upon the salt crystals and are rising through the acid and bursting. If the salt be placed in a flask (Fig. 85), the acid can be allowed to enter from time to time through the funnel. When the air has been displaced from the flask, the gas issues from the delivery tube. If the correct proportion of the acid is used, and only a gentle heat is applied, all that remains in the flask is a white solid, sodium-hydrogen sulphate (or sodium bisulphate)  $\text{NaHSO}_4$ :



The gas is extremely soluble in water and, being heavier than air, may be collected by upward displacement of the air in a jar.

The action described is the one which occurs in the laboratory.

\* An arrow pointing upward indicates escape as a gas, or solution of a solid; one pointing downward indicates precipitation.

When a double proportion of salt and a red heat are used, a second action occurs:



and sodium sulphate  $\text{Na}_2\text{SO}_4$  remains. In one or two factories in Europe this action is still employed, with furnace heat, in manufacturing sodium sulphate, from which sodium carbonate is afterwards prepared. The hydrogen chloride passes into a tower, down which water trickles over lumps of coke, and is dissolved. The aqueous solution is called hydrochloric acid or, in commerce, muriatic acid (Lat. *muria*, brine).

***Hydrogen Chloride from Other Chlorides and Other Acids.***

— The chlorides of other metals can be substituted for sodium chloride in this action, and all the more soluble ones give hydrogen chloride freely. Other chlorides are all more expensive, however, than common salt.

All acids contain the necessary hydrogen radical, and might offer it in exchange for the sodium in the salt, yet in practice no other acid works so well as does sulphuric acid. Most other acids contain much water, which dissolves the hydrogen chloride (see below). Concentrated phosphoric acid  $\text{H}_3\text{PO}_4$ , Aq acts slowly, giving primary sodium phosphate:

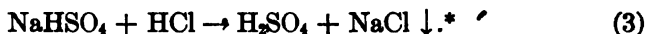


If various chlorides are used with the same acid, it will be found that the vigor of the actions is very different. In some, hydrogen chloride will be produced copiously without the assistance of heat. In others, there will be difficulty in showing that hydrogen chloride gas is produced at all. We must not hastily assume that this is owing to any greater chemical affinity in one case than another. More extensive experimentation will show that the *more soluble* chlorides as a rule give more vigorous effects than those which are less so (pp. 204, 220). Ammonium chloride with sulphuric acid would represent the former variety, while mercuric chloride with the same acid would represent the latter.

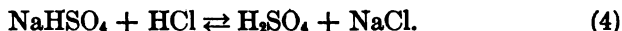
***The Molecular View of the Interaction of Sulphuric Acid and Salt.*** — One who has used the above method for making hydrogen chloride without reflection would not realize the complexity of the machinery by which the result is achieved. The means are apparently very simple. Yet the mechanical features of this experi-

ment, when laid bare, are extremely curious and interesting. A single fact will show the possibilities which are concealed in it.

If we take a *saturated* solution of sodium-hydrogen sulphate (that is, one containing the minimum amount of water), and add to it a concentrated solution of hydrogen chloride in water (concentrated hydrochloric acid), we shall perceive at once the formation of a copious precipitate. This is composed entirely of minute cubes of sodium chloride:



Now this action is nothing less than the precise reverse of (1), yet it proceeds with equal success. In fact, this chemical interaction is not only reversible (p. 153), but can be carried to completion in *either* direction. It is only in presence of a *large amount of water*, sufficient to keep both the hydrogen chloride and the salt in solution, that it stops midway in its career and is valueless for securing a complete transformation in either direction:



In an action which is reversible, if the *products* remain as perfectly mixed and accessible to each other as were the initial substances, because all are in solution (4), their interaction will continually undo a part of the work of the forward direction of the change. Hence, in such a case the reaction must, and does, come to a standstill while as yet only partly accomplished. But this was not the case with actions (1) and (3). Let us examine the means by which the premature cessation of each was avoided.

In (1) the salt dissolved to some extent in the sulphuric acid,  $\text{NaCl (solid)} \rightleftharpoons \text{NaCl (dissolved)}$ , and so, by contact of the two kinds of *molecules*, the products were formed. On the other hand, the hydrogen chloride, being almost insoluble in sulphuric acid, escaped as fast as it was formed:  $\text{HCl (dissolved)} \rightleftharpoons \text{HCl (gas)}$ . Hence, in that case, almost no reverse action was possible, and the double decomposition went on to completion. With all the sodium-hydrogen sulphate in the bottom of the flask, and most of the hydrogen chloride in the space above, the two products might as well have been in separate vessels so far as any efficient re-interaction was concerned. This plan, in which water is purposely excluded, forms therefore the method of making hydrogen chloride.



\* See footnote on p. 206.

In (3), on the other hand, the hydrogen chloride was taken *in aqueous solution*, and was mixed with a strong solution of sodium bisulphate. The acid was, therefore, kept permanently in full contact with the sodium bisulphate. It had, in this case, every opportunity to interact with the latter and no chance of escape. Every molecule of each ingredient could reach every molecule of the other with equal ease. Furthermore, the sodium chloride produced as a result of their activity is not very soluble in concentrated hydrochloric acid (far less so than in water), and so it came out as a precipitate:  $\text{NaCl (dissolved)} \rightleftharpoons \text{NaCl (solid)}$ . But this was almost the same as if it had gone off as a gas. It meant that the greater part of the salt was in the solid form. It was in a state of fine powder, it is true. But, in the molecular point of view, the smallest particle of a powder contains millions of molecules, and most of these are necessarily buried in the interior of a particle. Thus, the sodium chloride was no longer able to interact effectively molecule to molecule with the other product, the sulphuric acid. Hence, there was little reverse action to impede the progress of the primary one. Thus (3) is nearly as perfect a way of liberating sulphuric acid as (1) is of liberating hydrogen chloride.

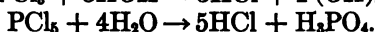
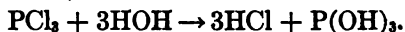
This discussion is given to illustrate the displacement of a chemical equilibrium, and to explain the method of preparing hydrogen chloride. It also throws an interesting light on **chemical affinity**, however. Considering action (1), by itself, we might reason that the hydrogen chloride was formed because the affinity of the hydrogen (H) for chlorine (Cl) was greater than for the sulphate radical ( $\text{SO}_4$ ). But, if we did so, then in action (3) we should be compelled to reason similarly that the preponderance of affinity was just the opposite. In point of fact, no conclusion about relative affinity can be drawn from these actions. The effects of affinity are here entirely subordinated by the effects of a purely mechanical arrangement (pp. 37, 127, 204), depending on solubility.

The egregious misconception that sulphuric acid is shown by this action to be "stronger" than hydrochloric acid was disposed of, so far as the science was concerned, half a century ago. But it survives in suburban chemical circles with remarkable tenacity. The fact, quaintly enough, is that real relation in respect to activity is just the reverse.

**Other Ways of Obtaining Hydrogen Chloride.** — Although never used for generating hydrogen chloride on a large scale, there is another important kind of action in which this substance is a product. When water acts upon the chlorides of non-metallic substances, like



sulphur, phosphorus, and iodine, a double decomposition (p. 20) occurs. Since water is always one of the interacting substances, this kind of change, — **a double decomposition involving water**, — is called **hydrolysis** (Gk. ὑδρῶν, water, and λύσις, the act of loosing). Thus, when a little water is added to one of the chlorides of phosphorus, hydrogen chloride is formed. Besides this substance, the trichloride gives phosphorous acid, and the pentachloride, phosphoric acid:



The water divides into the radicals H and OH, and the former unites with the more active non-metallic element in the substance (the Cl, in  $\text{PCl}_3$ ) and the hydroxyl with the other element.

A dissociation is a reversible decomposition of one substance into two or more (p. 148). Hydrolysis is an ordinary double decomposition or metathesis where water is one of the reagents. Yet it has been perversely named **hydrolytic dissociation** by many writers. A whole chapter might be devoted to the ingenuity with which chemists have misnamed many of the things with which they deal. Perhaps this tendency is a survival of the habit the alchemists had of using obscure and symbolical names for their materials to prevent the penetration of their secrets by uninitiated seekers after knowledge. Important facts and principles have been sedulously labeled with misleading titles, like: Water of crystallization, which has no more to do with crystallization than with color, density, or any other physical property; supersaturated solution, which, as a solution, is the same as any other; mass action, which has nothing to do with mass, but is concerned wholly with concentration; strong acid, which refers to activity and not power of resistance; reciprocal proportions, a law in which reciprocals of numbers play no part; downward displacement of air, when the air is displaced upwards, and so forth. Here there is an opportunity to confuse hydrolysis with electrolytic dissociation, and the beginner never fails to embrace it. Hydrolytic double decomposition would have been a correct, if somewhat clumsy term.

Often, when a steady stream of hydrogen chloride is required, concentrated hydrochloric acid is placed in a generating flask, and concentrated sulphuric acid is allowed to trickle into it from a dropping funnel. The hydrogen chloride is less soluble in diluted sulphuric acid than in water (see Solubility product) and escapes.

**Physical Properties.** — Hydrogen chloride is a colorless gas, which produces a suffocating effect when breathed.

Density (H = 1), 18.23

Weight of 22.4 l., 36.73 g.

Solubility in Aq. (0°), 50,300 vols. in 100

Crit. temp., +52°

Boiling-point (liq.), -83.7°

Melting-point (solid), -110°

The gas is one-fourth heavier than air. On account of its great solubility and the small vapor tension of its solution, it condenses atmospheric moisture into a fog of drops of hydrochloric acid. Its extreme solubility may be shown by filling a dry flask (Fig. 86) with the gas. The "dropper" contains water, and is closed at the tip with soft wax. A drop of water, expelled by pinching the "dropper," dissolves so much of the gas that the water is forced in by atmospheric pressure, like a fountain, through the longer tube. On account of its high critical point, it may be liquefied by pressure alone. Both in the gaseous and liquefied states it is a nonconductor of electricity. Its heat of solution (p. 203) is 17,400 calories.

On account of its high concentration, the solution may be looked upon as a mixture of liquefied hydrogen chloride and water. At  $15^{\circ}$  and 760 mm. 454.6 volumes of the gas dissolve in 1 volume of water, or 746 g. in 1 l. The mixture weighs therefore 1746 g. (42.7 per cent of HCl). Its sp. gr. is 1.215. The volume of the solution is given by the proportion  $1215 : 1 :: 1746 : x$ , in which  $x = 1.437$  l. Hence the addition of 454.6 liters of the gas has increased the volume by only 437 c.c. Now at  $15^{\circ}$  the sp. gr. of liquefied hydrogen chloride is 0.8320, and the volume of 746 g. is therefore  $746 \div 0.832 = 896$  c.c. So that, even if the substances had been mixed in liquid form, a considerable shrinkage would still have occurred (1000 c.c. Aq + 896 c.c. liq. HCl  $\rightarrow$  1437 c.c. HCl, Aq).

When the *concentrated* aqueous solution is heated, it is the gas and not the water which is driven out, for the most part. When the concentration has been reduced to 20.2 per cent the rest of the mixture distills unchanged at  $110^{\circ}$ . This occurs because, at this concentration, the gas enters into, and is carried off in, the bubbles of steam in the same proportion in which it is present in the liquid. With a concentration above 20.2 per cent, more hydrogen chloride enters the bubbles, with one below 20.2 per cent, more water. Hence, if a dilute solution is used, *water* is the chief product of distillation (about  $100^{\circ}$ ), but gradually the boiling-point rises and, when the concentration has reached 20.2 per cent once more, the same hydrochloric acid of **constant boiling-point** ( $110^{\circ}$  at 760 mm.), as it is called, forms the residue. It is thus impossible to separate by distillation the components of mixtures which behave in this way. This must necessarily be the case whenever, as here, the vapor tensions of the components

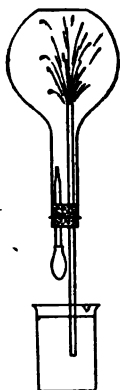


FIG. 86.

separately and those of all other mixtures are higher (and the b.-ps. lower) than that of one particular mixture. When, as is more often the case, one of the components has a vapor tension which is lower than that of the other and lower than that of any mixture of the two, this component will tend to remain behind, and separation can be effected. The separation of petroleum products (*q.v.*) from one another illustrates the common case (see under Alcohol for the third possibility).

The composition of the mixture having the minimum vapor tension varies with the external pressure, and so does the boiling-point. At 300 mm. the constant boiling liquid contains 21.8 per cent of hydrogen chloride and boils at 84°; at 1520 mm. it contains 19.1 per cent of the gas.

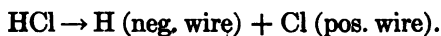
The common belief that hydrochloric acid of constant boiling-point is a definite compound is without foundation. Compounds do not vary in composition with changes in pressure in this manner. Aqueous solutions of hydrogen iodide, hydrogen bromide, and nitric acid behave in the same way. But solutions of oxygen, of ammonia, and of many liquids (*e.g.*, methyl alcohol) in water belong to the second of the two classes mentioned above, and the more volatile component often leaves the water entirely before much of the latter has evaporated.

**Chemical Properties.** — Hydrogen chloride is extremely stable, as we might expect from the vigor with which the elements of which it is composed combine (see p. 222). On being heated to a temperature of 1800° it dissociates into its constituents to a slight extent.

In the chemical point of view, it is on the whole rather an indifferent substance. When water is saturated with the gas at -22° a hydrate  $\text{HCl} \cdot 2\text{H}_2\text{O}$  crystallizes out. This decomposes into the same constituents when allowed to warm up again to -18°. Hydrogen chloride (the gas) has no action upon any of the non-metals, such as phosphorus, carbon, sulphur, etc. Many of the metals, however, particularly the more active ones, such as potassium, sodium, and magnesium, decompose it. Hydrogen is set free, and the chloride of the metal is formed ( $\text{K} + \text{HCl} \rightarrow \text{KCl} + \text{H}$ ). Hydrogen chloride unites directly with ammonia gas to form a cloud of solid particles of ammonium chloride ( $\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl}$ ). The liquefied gas has the same properties.

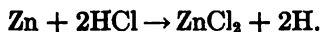
**Chemical Properties of Hydrochloric Acid.** — The solution of hydrogen chloride in water is an entirely different substance in its chemical behavior from hydrogen-chloride. It is **strongly acid**, turn-

ing blue litmus red. The gas and liquefied gas have no such property. The solution **conducts electricity**, as we have seen (p. 120), very well, and is decomposed in the process, giving hydrogen at the negative wire and chlorine at the positive wire:



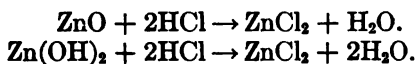
The gas and the liquefied gas are practically nonconductors.

The **metals** preceding hydrogen in the order of activity (p. 129), when introduced into hydrochloric acid, **displace the hydrogen** (p. 118), and form the chloride of the metal. In the case of zinc the action was represented by the equation:



The liquefied gas has no action upon zinc, and even its solutions in many other solvents show little activity. The solution in alcohol behaves like that in water. But the solutions in toluene, benzene, and other compounds of carbon and hydrogen, in many of which the gas is freely soluble, are hardly affected by the presence of zinc and other metals. These, and many other facts which we shall notice later (see Dissociation in solution), show that the condition of this substance in aqueous solution is peculiar.

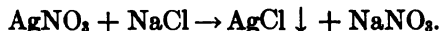
The aqueous solution of hydrogen chloride **interacts** rapidly with most **oxides and hydroxides of metals**, as, for example, those of zinc:



Here no hydrogen is obtained, since the oxygen in the oxide, and the hydroxyl in the hydroxide, unite with it to form water. In each case, however, the chloride of the metal is obtained. It may be noted in passing that all acids behave in a similar manner towards oxides and hydroxides, giving water and a compound corresponding to the chloride (see p. 218). Dilute sulphuric acid, for example, gives sulphates.

**Modes of Preparing Chlorides.**—In the preceding section three kinds of actions, each constituting a different **way of obtaining chlorides**, have been mentioned incidentally. There are two others. The simplest is the direct union of the element with chlorine ( $\text{Zn} + 2\text{Cl} \rightarrow \text{ZnCl}_2$ ). The other method is illustrated in the case of the precipitation of silver chloride (p. 20), by adding a solution of a

chloride to a solution of silver nitrate. Here the formation of the chloride occurred by exchange of another radical for chlorine:



The insoluble chlorides (see p. 226) can be made conveniently by this plan. The formation of the precipitates, for example that of silver chloride, is used as a **test** for the presence of a soluble chloride in the solution.

Double decompositions, like the action just mentioned, involving acids, bases, and salts (see below), are all reversible reactions. The fact that many of them proceed, nevertheless, to practical completion has already been explained at length (p. 208).

**Uses of Hydrochloric Acid.** — This substance is employed in cleaning metals, and in the manufacture of chlorides of metals. It is an important component of the gastric juice of the stomach, although the proportion is only about 1 part in 500.

**Precipitation.** — When two soluble substances are dissolved, separately, and the solutions are mixed, chemical interaction frequently occurs, as in the case of salt and silver nitrate (see also p. 209). If one of the products is insoluble, then a supersaturated solution of this product is at once produced. As a rule, this substance almost immediately becomes visible as a fine powder, called a **precipitate**, suspended in the liquid.

The insoluble product can often be recognized by its physical appearance, and so this sort of action is frequently used as a test for one of the *original* substances. Thus precipitates have often a distinctive **color**. Again, precipitates which are colorless, or have the same color, differ in appearance, and are described as **gelatinous**, **curdy**, **pulverulent**, or **crystalline**. In the first two cases, the precipitation is so sudden that there is not time for crystals to be formed, and the product is **amorphous** (Gk. *a*, priv.; *μορφή*, form). Thus silver chloride is curdy, and precipitated sodium chloride (p. 208) is crystalline.

**Salts.** — We have seen that an acid contains hydrogen as a radical (p. 117), and a base contains the radical hydroxyl OH (p. 149). The name **salts** is given to the class of substances, which contain a positive and a negative radical, **neither of which is hydrogen or hydroxyl**. For example, NaCl, Na<sub>2</sub>SO<sub>4</sub>, AgNO<sub>3</sub> are the formulæ of

salts. They are so named because they resemble common salt, in having two radicals, and entering readily into double decomposition.

Sodium-hydrogen sulphate  $\text{NaHSO}_4$  is classed as an **acid salt**, because it has a positive and a negative radical, and a hydrogen radical in addition.

### CHLORINE

Chlorine was first recognized as a distinct substance by Scheele (1774). He obtained it from salt by means of manganese dioxide, using the common method described below. It was for years supposed to be a compound containing oxygen, until Davy (1809–1818) demonstrated that it was an element.

**Occurrence.** — Chlorine does not occur free in nature. There are, however, many compounds of it to be found in the mineral kingdom. Sea-water contains a number of chlorides in solution. Nearly 2.8 of the 3.6 per cent of solid matter in sea-water is sodium chloride  $\text{NaCl}$ . During past geological ages the evaporation of sea-water has led to the formation of immense deposits of the compounds usually found in such water. Thus, at Stassfurt, such strata attain a thickness of over a thousand feet. Certain layers of these strata are composed mainly of sodium chloride, called by the mineralogist halite (rock salt). In other layers potassium chloride (sylvite), an indispensable fertilizer, and hydrated magnesium chloride (bischofite), and other compounds of chlorine, occur.

**Preparation.** — Chlorine cannot be obtained with the same ease as oxygen. There are only a few chlorides, such as those of gold and platinum, which lose chlorine when heated, and they are too expensive or difficult to make for laboratory use. We employ therefore methods like those used for the preparation of hydrogen (*cf.* p. 122). We may (1) decompose any chloride by means of electricity, just as, to get hydrogen, we electrolyzed a dilute acid (p. 120). Or (2) we may take some inexpensive compound of chlorine, such as hydrogen chloride  $\text{HCl}$ , and by means of some simple substance which is capable of uniting with the hydrogen, — here oxygen serves the purpose, — secure the liberation of the chlorine. Or (3) — and this turns out to be the most convenient laboratory method — we may use a more complex action.

**Electrolysis of Chlorides.**— Hydrogen chloride and those chlorides of metals which are soluble in water are all decomposed when a current of electricity is passed through the aqueous solution. They yield chlorine at the positive electrode. The other constituent, the hydrogen (Fig. 87), manganese, or whatever it may be, migrates towards

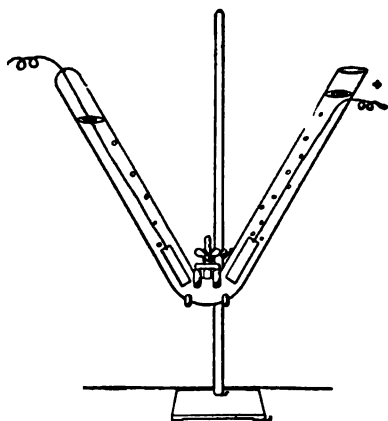
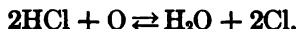


FIG. 87.

the negative wire. To decompose hydrochloric acid an electromotive force of at least 1.31 volts is required. Since the chlorine is soluble in water, the effervescence due to its release is not noticeable until the liquid round the electrode has become saturated with the gas:  $\text{Cl (dissolved)} \rightleftharpoons \text{Cl (gas)}$ . The shape of the apparatus keeps the two products from mingling. The presence of the chlorine in the liquid at the positive end may be shown by a suitable test (pp. 89 and 223).

In commerce chlorine is now obtained chiefly by this method, sodium chloride or potassium chloride being the source of the element. Electrodes of artificial graphite are used, as most other conductors unite with the chlorine. The potassium or sodium, as the case may be, travels towards the negative electrode, but is not liberated. Instead, potassium or sodium hydroxide (*q.v.*) accumulates in the solution round the plate and hydrogen escapes. The chlorine is released at the positive electrode, as usual. The hydrogen, the hydroxide and the chlorine all find commercial applications. The chlorine is either liquefied by compression in iron cylinders or employed at once for making bleaching powder (*q.v.*).

**Action of Free Oxygen on Chlorides.**— Sodium chloride is the cheapest source of chlorine, but oxygen does not interact with it even at a high temperature. Hence the chlorine must first be transferred to some other form of combination. By treating the sodium chloride with sulphuric acid, therefore, the chlorine is first transferred into combination with the hydrogen of the acid, giving hydrogen chloride (p. 206). In order to liberate chlorine from this compound, we may combine the hydrogen with oxygen obtained from the air:



The two gases interact so slowly, however, that a contact agent must be employed. The mixture of air and hydrogen chloride is passed over pieces of heated pumice-stone or broken brick, previously saturated with cupric chloride solution (Fig. 88). A temperature of about  $370^{\circ}$  is used. Furthermore, the action is reversible (read the equation backwards) and equilibrium is reached when 80 per cent of the hydrogen chloride has been decomposed. Hence 20 per cent

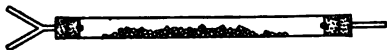


FIG. 88.

of this gas passes on unchanged. Only 80 per cent of the hydrogen chloride and oxygen are changed into steam and chlorine, because the latter substances are continuously interacting to reproduce hydrogen chloride and oxygen. If one substance (the steam or the chlorine) could be separated from the other (p. 208), to prevent the backward action, the yield would be raised to 100 per cent. But even a very partial separation of two gases requires elaborate apparatus and complete separation is practically impossible. In the product, therefore, the chlorine is mixed with steam, as well as with a very large volume of nitrogen which entered with the oxygen, so that for making the pure substance this method (**Deacon's process**) is quite unsuitable. Bleaching powder (*q.v.*), however, can be made by this process.

Using the same principle, magnesium chloride may be heated in a stream of air, when the oxide of magnesium is formed and chlorine is given off:  $\text{MgCl}_2 + \text{O} \rightarrow \text{MgO} + 2\text{Cl}$ . The oxide of magnesium can then be treated with hydrochloric acid to regenerate the chloride, which in turn may be subjected once more to the action of oxygen. The process is thus a continuous one.

The above action is spoken of as an oxidation. It is true that no oxygen is actually introduced into the hydrogen chloride as a whole. The removal of hydrogen from combination with the chlorine is, however, the first step towards the introduction of oxygen into combination with the latter, which is essentially an oxidation.

**Action of Combined Oxygen upon Chlorides.**—The best laboratory method for making chlorine is to place some solid potassium permanganate in a flask, arranged like that in Fig. 89. Concentrated hydrochloric acid (an aqueous solution of hydrogen chloride), diluted with one-third of its volume of water, is allowed to fall upon the compound drop by drop from the dropping funnel. The action is very rapid, the acid is exhausted almost as fast as it falls, and so the stream of gas can be stopped by simply closing the stopcock. The



gas is passed through a washing bottle containing water, in order to remove any hydrogen chloride which may be carried over. It may be dried, if necessary, in a second washing bottle containing concentrated sulphuric acid. It cannot be collected over water on account of its solubility, so that jars are usually filled with it by upward displacement of air.

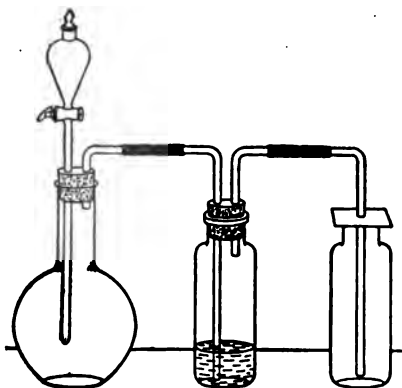
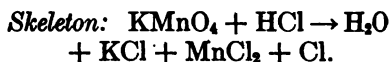
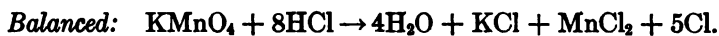


FIG. 89.



The  $\text{O}_4$ , being all converted into water, requires  $8\text{H}$ , and therefore  $8\text{HCl}$ , for the action. The two metals, potassium and manganese, give their respective chlorides,  $\text{KCl}$  and  $\text{MnCl}_2$ . This uses  $3\text{Cl}$ , and hence  $5\text{Cl}$  remains over to be liberated:

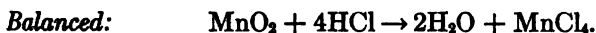


The combined oxygen of the permanganate has oxidized the hydrogen chloride, just as did the free oxygen in Deacon's process.

**Other Means of Oxidizing Hydrogen Chloride.**—Many other compounds of oxygen with metals interact with hydrochloric acid to give free chlorine. Lead dioxide  $\text{PbO}_2$ , potassium chlorate  $\text{KClO}_3$ , potassium dichromate  $\text{K}_2\text{Cr}_2\text{O}_7$ , and manganese dioxide  $\text{MnO}_2$ , are of this nature. The last, being inexpensive, is commonly used in making chlorine. Being an insoluble substance, however, the manganese dioxide acts much more slowly than does the potassium permanganate, which is soluble. A large amount of the materials, and the aid of heat, are required to secure a rapid stream of chlorine.

**Manganese Dioxide and Hydrogen Chloride.**—The action of manganese dioxide upon hydrochloric acid is an instructive one. It is a **general rule**, of which we shall meet many applications, that **when an acid interacts with an oxide of a metal**, there are two constant features in the result, namely: (1) **The oxygen of the oxide combines with the hydrogen of the acid to form water**, and (2) **the metal of the oxide combines with the acid radical of the acid according to the valences of each**. Here the skeleton equation should

be  $\text{MnO}_2 + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{MnCl}_2$ . With  $\text{O}_2$ , to form water,  $4\text{HCl}$  is required, and the product is  $2\text{H}_2\text{O}$ . Hence the equation is



This is what happens in the first place. The products actually obtained, however, are water, manganous chloride  $\text{MnCl}_2$ , and chlorine. The manganese tetrachloride is decomposed by the heating, the chlorine escapes, and the other two products remain in the vessel.

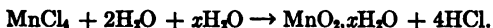


We owe the chlorine to the fact that the tetrachloride is unstable.

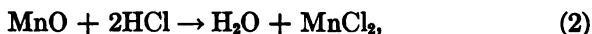
When the mixture is surrounded by ice and saturated with chlorine, it can be shown that it contains the tetrachloride. If it is quickly poured into water, hydrated manganese dioxide is precipitated (Wacker). The decomposition of the tetrachloride is reversible:



and is driven back by the excess of chlorine. The tetrachloride is hydrolyzed by water:

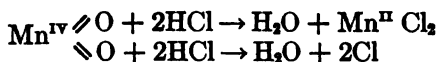


The action (1) is of a type very common in chemistry. It is more complex even than double decomposition (p. 20), and, unlike this, its results cannot be anticipated by guessing. If we had used manganous oxide  $\text{MnO}$ , we should have had a double decomposition:



but we should have got no chlorine. Perhaps the simplest way to describe the difference between these two actions is in terms of the valence of the manganese. In  $\text{Mn}^{\text{IV}}\text{O}_2$  the element is quadrivalent. This means that its atomic weight professes to be able to hold four atomic weights of a univalent element. The four valences of oxygen ( $2\text{O}^{\text{II}}$ ) can do the same thing. In equation (1) the oxygen fulfils this promise by taking  $4\text{H}^{\text{I}}$ . But the  $\text{Mn}^{\text{IV}}$  can hold only  $2\text{Cl}^{\text{I}}$ , permanently, and lets the other  $2\text{Cl}^{\text{I}}$  go free. In other words, the *valence* of the atomic weight of *manganese changes* in the course of the action. In equation (2), on the other hand, the manganese is bivalent to start with ( $\text{Mn}^{\text{II}}\text{O}^{\text{II}}$ ), and is able to retain the amount of chlorine ( $2\text{Cl}^{\text{I}}$ ) equivalent to  $\text{O}^{\text{II}}$ . Actions like that of manganese dioxide in (1) are classed as oxidations. The hydrogen chloride, or rather half

of it, is oxidized. A graphic mode of writing may make this remark clearer:



The upper half is a double decomposition, the lower an oxidation by half the combined oxygen of the dioxide.

In practice, instead of employing aqueous hydrochloric acid we frequently use the materials from which it is prepared, namely, common salt and concentrated sulphuric acid (p. 206), along with the manganese dioxide. Under those circumstances, the action appears more complex, but is simply a combination of the two chemical changes, and is represented by the equation:



**Kinetic-Molecular View of these Actions.**—In preparing chlorine with manganese dioxide, the gas is produced rather slowly. The situation is that we have placed together manganese dioxide in a granular form and water which contains hydrogen chloride in solution. The dioxide is very insoluble in water, and consequently its molecules, which must dissolve before they can meet the acid, are present in small quantities:  $\text{MnO}_2 (\text{solid}) \rightleftharpoons \text{MnO}_2 (\text{dissd})$ . The finer the pulverization, and the larger the amount of the oxide, the less will be the delay from this cause. On the other hand, the acid contains originally only about one molecule of hydrogen chloride for every five of water and, as the former is used up, the scarcity of the active substance becomes greater.

Again, we heat the mixture on a water bath so as to hasten the process (p. 93) by raising the temperature to about  $90^\circ$ . When we prepared oxygen, we forced the temperature up with a naked Bunsen flame until, at about  $300^\circ$ , a sufficiently rapid stream of the gas was secured. The iron and sulphur (p. 16) we raised nearly to a red heat. Here the conditions make stronger heating impossible. No aqueous solution of hydrogen chloride can be raised above  $110^\circ$ , the maximum boiling-point (p. 211). But we must not carry the heating so far as  $110^\circ$ , because even below this point the concentrated acid gives off gaseous hydrogen chloride freely. If we did, we should contaminate our chlorine and at the same time lose a part of one of the ingredients on which the action depends. Intelligent chemical work always demands a careful consideration of purely physical facts of this description.

On the other hand, when potassium permanganate is employed (p. 217), the chlorine is evolved very rapidly. The permanganate is fairly soluble in the cold (6.5 : 100 Aq at 15°), and becomes rapidly more soluble as the heat of the reaction raises the temperature of the liquid. Then, too, the permanganate is a more active oxidizing agent, at equal concentrations, than is manganese dioxide, and so attacks the hydrochloric acid more rapidly.

**Physical Properties.** — Chlorine differs from the gases we have encountered so far in having a strong greenish-yellow tint (Gk. *χλωρός*, pale green), a fact which gave rise to its name, and having a powerful, irritating effect upon the membranes of the nose and throat.

Density (H = 1), 35.79

Boiling-point (liq.), -33.6°

Weight of 22.4 l., 72.13 g.

Melting-point (solid), -102°

Solubility in Aq (20°), 215 vols. in 100

Vap. tension (liq.) 0°, 3.66 atmos.

Crit. temp., +146°

Vap. tension (liq.) 20°, 6.62 atmos.

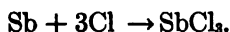
Since a liter of air weighs 1.293 g., chlorine (wt. 1 l., 3.22 g.) is two and a half times heavier. In solubility it stands between slightly soluble gases, like oxygen and hydrogen, and those which are extremely soluble. It can be collected over hot water or a strong solution of salt.

It was first liquefied by Northmore (1806). The critical temperature (p. 166) is exceptionally high (146°), so that at all ordinary temperatures the gas can be liquefied by compression alone. It forms a yellow liquid which, contained in steel cylinders, is now an article of commerce. On being cooled below -102°, it gives a pale-yellow solid.

**Chemical Properties.** — Chlorine is at least as active a substance as is oxygen. It presents a more varied array of chemical properties than does that element (see below). The binary compounds are called **chlorides**.

**Combines with Metals.** Powdered antimony (cold), when thrown into chlorine, unites with it to form the chloride  $\text{SbCl}_3$ , which appears partly as vapor and partly as glowing particles.

**Balanced:**



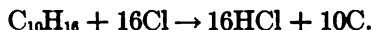
Copper, in the condition of thin leaf commonly used for gilding (Dutch-metal), catches fire when thrust into the gas, giving a fog of solid cupric chloride  $\text{CuCl}_2$ . Sodium burns brilliantly, giving a cloud of sodium chloride. The union of a metal like sodium and

a colored, irritating gas to give a mild household article, like common salt, illustrates the extraordinary nature of chemical change. All the familiar metals, with the exceptions of gold and platinum, combine readily with chlorine.

When metals (like copper and iron) and chlorine are first thoroughly freed from moisture, combination no longer occurs. A trace of water vapor is required in these, as it is in many other chemical actions, as a contact agent. Hence, the chlorine, before being compressed into steel cylinders, must be freed entirely from water vapor (see Detinning).

**Combines with Hydrogen.** A jet of hydrogen burns vigorously in chlorine, producing hydrogen chloride. The presence of this product may be recognized at once, because, while chlorine in contact with moist breath gives no cloud, hydrogen chloride (*q.v.*) produces a dense fog. The union of the gases, when a mixture of them is kept cold and in the dark, is too slow to be perceived. On exposure to diffused light, however, they unite slowly, while a sudden flash of sunlight or the burning of a magnesium ribbon causes instant explosion. The function of the light here is entirely different from that in the decomposition of silver chloride (p. 19). In the latter case light was used to maintain the change, which comes to a stop whenever the light is withdrawn: the action was endothermal and consumed energy. The union of hydrogen and chlorine is highly exothermal, and a minimum of light only is needed to start it (pp. 94-95). The action of the light is catalytic.

**Interacts with Compounds Containing Hydrogen.** When a lighted taper is plunged into chlorine it continues to burn, but a dense cloud of soot (free carbon) rises from the flame. Blowing the breath into the jar then gives the fog which shows the presence of hydrogen chloride. Thus the presence of hydrogen and carbon in the wax is proved. We learn, also, that chlorine has little tendency to combine with carbon, for this element goes free. A few drops of warm turpentine, poured upon a strip of paper, when placed in chlorine give a violent reaction and a cloud of finely divided carbon bursts forth.

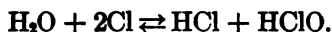


**Elements Displaced by Chlorine.** The action on turpentine is a displacement of the carbon by the chlorine. Of the same nature is the action of chlorine upon potassium iodide KI, dry or in solution.



The iodine, when moist, is deep brown in color. A mere trace of chlorine, liberating a trace of iodine, gives no visible effect. But if some starch is present, even a trace of free iodine yields a deep blue color. This reaction is used as a test for chlorine, for free iodine from any source, and for starch (p. 5). To test for chlorine, strips of filter paper, dipped in starch emulsion (starch boiled with much water and cooled) to which a few drops of potassium iodide have been added, are used. Combined iodine, as in potassium iodide, has no effect upon starch. Combined chlorine, as in sodium chloride, has no action upon the prepared strips of paper — free chlorine is required.

**Action upon Water.** We have seen that chlorine seizes the hydrogen in turpentine. We have also learned that it combines with the hydrogen in steam, reversing Deacon's process to the extent of 20 per cent. It also acts upon cold water, when dissolved in the latter, although in a similarly incomplete way. The substances formed are hydrochloric acid and hypochlorous acid  $\text{HClO}$ :



With half-saturated chlorine-water at  $10^\circ$  — that is, water containing an equal volume of chlorine gas — 33 per cent of the chlorine is changed into the acids. When one-fifth saturated ( $10^\circ$ ), 52 per cent is changed into the acids, and when one-tenth saturated, 73 per cent (Jakowkin). The percentages become greater above  $10^\circ$ . Thus, chlorine-water (the solution) is a mixture containing dissolved chlorine and two acids. Hypochlorous acid (*q.v.*) is of especial interest because it is a very active substance, with powerful oxidizing qualities, and bleaches dyes by decomposing them.

The action comes to a standstill when one-third completed, because the two acids interact to reproduce chlorine and water (read the equation backwards). The action is reversible. When the solution is exposed to sunlight, the hypochlorous acid decomposes and oxygen gas is liberated and escapes:



Since this removes the hypochlorous acid, on whose interaction with the hydrogen chloride the reverse action depends, the forward action proceeds under continuous illumination gradually to completion. Hence the aqueous solution of chlorine must be kept in the dark, since otherwise, after a time, a dilute solution of hydrogen chloride alone remains.

The reader should note here the displacement of the equilibrium, a chemical one in this case, in consequence of the annulment of one of the opposing tendencies (p. 170). Through the destruction of the hypochlorous acid, one of the tendencies, namely, that represented in the backward action, becomes inoperative. The forward action is not itself assisted, but it is no longer impeded, and so proceeds to completion.

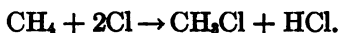
The so-called bleaching action of "chlorine" is almost always the result of oxidation of the coloring matter by hypochlorous acid (*q.v.*). Chlorine and the dye in the cloth, even when only moderately dry, show no tendency to interaction. This may be demonstrated by collecting some chlorine in a stoppered bottle in the bottom of which a little concentrated sulphuric acid stands. A piece of colored calico may be attached by a pin to a cork stuck in the bottom of the stopper and so suspended in the gas. After twenty-four hours no action will be found to have occurred. Yet if the rag is first moistened, the bleaching is almost instantaneous. Hence this bleaching action is treated under the properties of hypochlorous acid.

**So-called "Nascent Oxygen."** — The oxidizing action of chlorine-water is commonly attributed to "nascent oxygen" — oxygen in the state of being born. It was supposed that the chlorine preëmpted the hydrogen of the water, without actually combining with it, and so left the oxygen in a distracted condition in which it was more active than free oxygen! But all this speculation occurred before we knew that there was hypochlorous acid in chlorine-water. A pure solution of this acid performs all the oxidations that chlorine-water can bring about. So that, since we have now to choose between a substance we know to be present, and to be perfectly capable of doing the work, and an imaginary, ill-defined entity, the scientific method naturally demands that we attribute the effect to the substance. In this connection, the correct name for "nascent oxygen" is, therefore, hypochlorous acid.

It is, in any case, time that the term, and the idea of "nascent oxygen" should be eliminated from the science. This material is imaginary — it has never been isolated or studied quantitatively. If it is an allotropic form of oxygen, it must have properties and a degree of activity that can be defined quantitatively. But this cannot be done, because it has not always the same activity. Thus, if all oxidizing agents perform their oxidizing by means of "nascent oxygen," it is curious that hypochlorous acid oxidizes hydrochloric acid instantly and easily, while hydrogen peroxide does not, also that chloric acid  $\text{HClO}_3$  oxidizes hydrochloric acid rapidly, while perchloric acid  $\text{HClO}_4$  does not. (For explanation of oxidation by oxidizing agents, see pp. 314, 321.) If we mean that, when the free elements are not present and yet compounds containing them interact, we must assume that the elements are in the nascent condition, then we should be consistent, and explain the action of sulphuric acid on sodium chloride as being due to nascent chlorine and nascent hydrogen! All double decompositions would demand the same mode of explanation! Finally, since every oxidation is accompanied by a reduction, when we assume the presence of nascent

oxygen, to be consistent, we ought to assume the presence of nascent hydrogen also: each such case involves a twin birth. The conception will not bear careful examination.

**Action by Substitution.** When actions like that on turpentine—that is on compounds containing carbon and hydrogen—are moderated by altering the conditions, the decomposition is not so complete. Using a lower temperature is effective. Thus, if methane  $\text{CH}_4$  (marsh-gas), the chief component of natural gas, is mixed with chlorine and exposed to sunlight, a slower action occurs, of which the first stage consists in the removal of one unit weight of hydrogen and the substitution of chlorine for it according to the following equation:



The process may continue further by the substitution\* of chlorine for the units of hydrogen one by one until carbon tetrachloride  $\text{CCl}_4$  is finally formed.

The action on water (previous section) is a substitution.

**Combines with Non-metals.** Phosphorus burns in chlorine with a rather feeble light, producing primarily phosphorus trichloride  $\text{PCl}_3$ , a liquid (b.-p.  $74^\circ$ ). If excess of chlorine is present, then, as the trichloride cools, it combines to form the solid pentachloride  $\text{PCl}_5$ . Sulphur, when heated, unites more slowly, giving sulphur monochloride  $\text{S}_2\text{Cl}_2$ , a liquid used in vulcanizing rubber. Chlorine does not combine directly with carbon, nitrogen, or oxygen, although compounds with those elements can be made indirectly. With the helium group of elements (*q.v.*), it forms no compounds.

**Combines with Compounds.** Chlorine unites with many compounds. Thus, one of the oxides of carbon, carbon monoxide  $\text{CO}$ , when mixed with chlorine and exposed to sunlight gives drops of a volatile liquid (b.-p.  $8.2^\circ$ ) known as phosgene  $\text{COCl}_2$ .

\* **Substitution** resembles displacement (p. 18) in that an element and a compound interact, and the element takes the place of one unit in the composition of the latter. In the above action, one unit of chlorine takes the place of one unit of hydrogen. But *the latter is not liberated*; it combines with another unit of chlorine. The action resembles double decomposition, excepting that one of the substances is not a compound, but a diatomic element. The name used is intended to fix the attention on the *compound* and on the fact that one unit has been *substituted* for another in it. This conception is a favorite one in the chemistry of compounds of carbon.



When chlorine-water is cooled with ice, a compound, **chlorine hydrate**  $\text{Cl} \cdot 4\text{H}_2\text{O}$  crystallizes out. Faraday (1823) placed this substance in the closed limb of a  $\Lambda$ -tube, sealed the open end, and placed the empty limb in ice and water (Fig. 90). When the hydrate was gently warmed, chlorine gas was given off and was liquefied by its own pressure in the cold part of the tube.

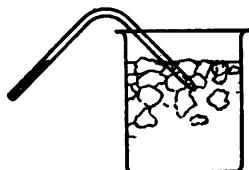


FIG. 90.

### *Chemical Relations of the Element.\**

— In the chlorides, an atomic weight of chlorine is equivalent to one atomic weight of hydrogen or of sodium. The element is, therefore, **univalent** (p. 131). It never shows any higher valence than this save in its oxygen compounds (see Chap. XXIII). The oxides of chlorine interact with water to give acids, and the element is, therefore, to be classed as a **non-metallic element** (p. 150). It belongs to that **group** of the non-metallic elements called the **halogens**, as a consideration of some others of its relations will show (see Chap. XIV and Periodic system).

**Uses of Chlorine.** — Large quantities of chlorine are manufactured for the preparation of bleaching materials and disinfecting agents. In disinfection, the minute germs of disease and putrefaction are acted upon by the hypochlorous acid formed by the interaction of chlorine with water, and instantly their life is destroyed.

**Chlorides.** — The chlorides are described individually under the other element which each contains. The majority of the chlorides of the metals are easily soluble in water. The only familiar exceptions are silver chloride  $\text{AgCl}$ , mercurous chloride (calomel)  $\text{Hg}_2\text{Cl}_2$ , cuprous chloride  $\text{CuCl}$ , aurous chloride (one of the chlorides of gold)  $\text{AuCl}$ , thallous chloride  $\text{TlCl}$ , and ordinary lead chloride  $\text{PbCl}_2$ . The last of these is on the border line as regards solubility. An appreciable

\* In accordance with the distinction that must be drawn (p. 23) between the element as a variety of matter in combination, and the elementary substance or free form of the element, and to avoid a common source of confusion, we shall always give only the behavior of the elementary *substance* under the title *chemical properties*. The characteristics which distinguish the *compounds* of the element, as a class from, or relate them as a class to the compounds of other elements will then appear in a separate section under the title "chemical relations" (see Chap. XIV, first section and Chap. XXII, Periodic system, fifth section).

amount dissolves in cold water, and a considerable amount in boiling water. For the various modes of preparing chlorides, see p. 213.

**Composition of Hydrogen Chloride.** — Being now familiar with both hydrogen and chlorine, we may take up the proportions by weight in which they combine, and also the proportions by volume in which the constituents unite, and the relation of this to the volume of the resulting hydrogen chloride.

The proportion of hydrogen to chlorine by weight in this compound is 1 : 35.18. Taking the atomic weight of hydrogen 1.008, so as to harmonize that of chlorine with  $O = 16$ , the standard scale for atomic weights, the ratio becomes 1.008 : 35.46.

The proportion by volume in which the constituents unite, and the relation of this to the volume of the resulting hydrogen chloride, may easily be shown in several ways. The decomposition of the solution of hydrogen chloride in water by means of the electric current proves that the gases are liberated in equal volumes.

The apparatus in Fig. 44 (p. 120) cannot be used to show this, because, under the increasing pressure due to the displacement of the liquid into the higher bulb, the chlorine becomes more and more soluble, and its volume therefore falls progressively more and more below what it should be.

Brownlee's apparatus for demonstrating this is shown in Fig. 91. The central part is the same as in Fig. 44, but, when the three-way stopcock is closed, the gases go to right and left, and displace the liquid in two outside tubes (water in one and chlorine-water in the other). The equal rate at which this takes place on both sides proves that the gases are generated in equal volumes.

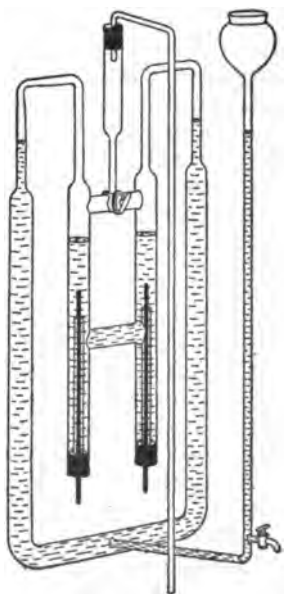


FIG. 91.

In order to ascertain the relation between the volumes of the constituents and *that of the product*, we may unite the gases and find out whether any change in volume occurs. A tube with thick walls (Fig. 92) is filled with the mixed gases obtained by electrolysis. By

dipping one end of the tube under mercury and opening the lower stopcock, it is seen that no gas leaves and no mercury enters. After the mixture has been exploded, by the light from burning magnesium, the same test is repeated with the same result. The pressure has therefore remained equal to that of the atmosphere. Hence there has been no change in volume as the result of the union. It appears therefore, that:



Fig. 92.

**1 vol. hydrogen + 1 vol. chlorine  $\rightarrow$  2 vols. hydrogen chloride,**  
a result in harmony with Gay-Lussac's law (p. 157).

Another way of demonstrating the equality in the volumes of the hydrogen and chlorine is to fill a wide tube, closed at each end by a stopcock, with the mixed gases arising from electrolysis of hydrochloric acid. When the air has been entirely displaced, the stopcocks are closed. The gases which the tube then contains are present very nearly in the proportions in which they are liberated from the decomposition of the substance. By introducing a small amount of potassium iodide solution, the chlorine is removed ( $\text{KI} + \text{Cl} \rightarrow \text{KCl} + \text{I}$ ). It forms potassium chloride, which remains dissolved in the water, and free iodine, which dissolves in the excess of potassium iodide solution. Neither product is gaseous under the circumstances, so that the volume of the mixed gases diminishes by the amount of chlorine removed. If the stopcock is now opened under water, the latter enters and fills half the length of the tube. The remaining gas is easily shown to be hydrogen.

To show that the volume of the hydrogen chloride is twice that of either constituent in the free condition, an alternative method is likewise available. We may completely fill a long test-tube with hydrogen chloride, introduce into it quickly some sodium dissolved in mercury, and, after agitation, open the closed tube under mercury. The sodium gives sodium chloride and free hydrogen, and it is found that the mercury enters so as to fill one-half of the tube. Since from this experiment we learn that the hydrogen occupies half the space of the hydrogen chloride, and from the previous experiment we know that the volume of hydrogen is equal to that of the chlorine, we conclude that two volumes of mixed hydrogen and chlorine would give two volumes of hydrogen chloride.

**Classification of Chemical Interactions and Exercises Thereon.**—So far we have defined ten more or less distinct kinds of chemical change: **Combination** (p. 12), **decomposition** (p. 17), **dissociation** (p. 148), **displacement** (p. 18), **substitution** (p. 225), **double decomposition** (p. 20), **hydrolysis** (p. 210), **oxidation** (pp. 91, 217, 218), **reduction** (pp. 92, 127), and **electrolysis** (p. 121). In one or two of these classes all the actions are **reversible**, in others some are reversible and some are not. Illustrations of every one of these will be

found in the present chapter. The classes are not mutually exclusive. Some actions belong to one class or another according to our point of view at the moment. The ability readily to classify each phenomenon, as it comes up, requires precisely that grasp of the framework of the science which the reader must seek speedily to attain. For example, let him classify the following actions: 1. Action of heat on chloroplatinic acid; 2. of potassium on water; 3. of heat on potassium chlorate; 4. of chlorine on metals; 5. of chlorine on turpentine; 6. of chlorine on potassium iodide; 7. of chlorine on methane; 8. of carbon monoxide and chlorine; 9. of sunlight on hypochlorous acid; 10. of sulphuric acid on salt; 11. of zinc oxide and hydrochloric acid; 12. of zinc on hydrochloric acid.

13. Expand the explanation of the tendency of hydrogen chloride to fume in moist air (p. 211).

14. Explain the interaction of steam and iron (p. 128) on mechanical principles similar to those used in describing how hydrogen chloride is formed from salt and sulphuric acid (p. 208).

15. In the interactions of potassium permanganate and of manganese dioxide, respectively, with hydrochloric acid, what fractions of the whole chlorine are liberated? What are the commercial advantages of the use of salt and sulphuric acid with the manganese dioxide?

16. What are the relative volumes of the gaseous interacting substances and products in the following reactions: (a) turpentine vapor and chlorine; (b) methane and chlorine; (c) phosphorus vapor and chlorine; (d) carbon monoxide and chlorine.

17. In view of the explanations given, can you define the general nature of the "other substances" (p. 218) which may be used to oxidize hydrochloric acid?

#### SUMMARY OF PRINCIPLES

It may be useful at this point partially to summarize the principles (general facts) of chemistry so far as they have been developed in the preceding chapters. These principles are given under fourteen heads below. They are stated as far as possible strictly in terms of facts, since hypotheses are not integral parts of chemistry, but are scaffolding temporarily employed to facilitate the erection of the structure of the science. In a later chapter (Chap. XV), some other important principles will be summarized in like manner. To secure more strictly logical arrangement than has seemed advisable in the text, two conceptions which have already been dealt with are held over to the second half of the summary, namely, 17 (valence) and 21 (chemical relations of elements). The reader should give careful thought to the various points, many of which, in a backward view, will be found

to have become susceptible of improved statement. We begin the series with the most fundamental fact of all, — the one without which no chemical work would be possible:

1. Each substance has its own set of specific physical properties. By means of these it is recognized and, when necessary, separated from other substances (p. 3).

2. Substances are either simple (elementary), containing only one kind of matter, or compound, containing more than one kind of matter (p. 23).

3. In all chemical actions (excepting "internal rearrangements"), changes in the material composition of bodies occur (p. 21).

4. In chemical actions there is no change in the total mass of the system (p. 52).

5. Each substance has a definite material composition by weight (p. 54).

6. The proportions by weight in which all chemical combinations take place can be expressed in terms of small integral multiples of fixed numbers, which may be called combining weights, one for each element. That weight of each element which combines with 8 parts of oxygen is called the equivalent weight and has the properties of a combining weight (pp. 61, 63).

7. The proportions by volume in which all chemical interactions involving substances in the gaseous condition take place are expressible by small integers (p. 157).

8. From 6 and 7 it follows that the equivalent weights of all substances occupy, in the gaseous condition and at the same temperature and pressure, volumes which are either equal or stand to one another in the ratio of small integers (p. 158).

9. In every chemical phenomenon a transformation of energy occurs. This results in a redistribution of the internal energy in the substances concerned, and also in an increase or a decrease in the free internal energy in the system (p. 35).

10. In chemical phenomena there is no actual loss or gain, but only transformation of energy (p. 32).

11. Interactions which proceed spontaneously are in general those in which the free energy is transformed into some other variety or varieties of energy (p. 35).

12. Each substance has its own set of chemical properties, such as:

(a) Affinity: the given substance can or can not interact with such and such elementary and compound substances.

(b) Relative activity of the systems in (a). This is measured quantitatively by: ( $\alpha$ ) Relative speed under like conditions (see 13, 14, 18); ( $\beta$ ) Relative heat developed, when actions compared can be carried out so that all conditions are alike; ( $\gamma$ ) Relative E.M.F. of cell when the action is so arranged as to give electricity (pp. 128, 98, 37).

13. The speed of every interaction is increased by raising the temperature (p. 93).

14. The speed of interactions is increased or decreased by catalytic agents, each of which is individual in the kind and amount of its effect (p. 97).

## CHAPTER XII

### MOLECULAR WEIGHTS AND ATOMIC WEIGHTS

AVOGADRO's law (p. 163) has proved to be by far the most suggestive and fruitful of all the conceptions developed from the kinetic-molecular theory. We are now in a position to discuss several of its most important applications. These concern more particularly the measurement of the relative weights of the molecules of different gaseous substances, and the determination of the most convenient magnitudes for the chemical unit weights (atomic weights; cf. p. 63).

**Meaning of Avogadro's Hypothesis.** — First, we must understand clearly what is implied in the statement that: In equal volumes of all gases, at the same temperature and pressure, there are equal numbers of molecules. It means that, for instance, at 100° and 760 mm., in specimens of all gases, the average spacing of the molecules is identical. This condition is independent of the nature of the gas — for example, whether it is a simple or a compound substance, like oxygen and carbon dioxide, respectively, or a mixture, like air. It means that when, at some fixed temperature, we fill the same vessel with a number of different gases or gaseous mixtures successively, the number of molecules that it will hold at a pressure, say, of one atmosphere will always be the same. If we take care to keep temperature and pressure the same, the equality in the number of molecules that will enter the jar will take care of itself automatically. In what follows, to avoid continual repetition, standard conditions (0° and 760 mm.) are assumed unless other conditions are specifically mentioned.

This statement would be *strictly* true only in the case of gases, if such existed, which behaved in ideal accord with the laws of Boyle and Charles. Since, however, in all gases, with the exception of hydrogen, a certain tendency to cohesion between molecules is distinctly noticeable and its amount varies from gas to gas, the density with which the molecules are packed is not *precisely* the same in any two of them (p. 164). Hence, Avogadro's law is not perfectly realized in any known gases. In the case of hydrogen, for example, a very slight divergence from the behavior of an ideal gas exists, and in the case of chlorine it amounts

to about  $1\frac{1}{2}$  per cent, and is quite conspicuous. This slight irregularity in the packing of the molecules, however, does not interfere with the application of this law in chemistry.

**Two Kinds of Laws in Science.** — It will have been observed that the laws of science may be divided into two kinds. Some, like those of conservation of mass and of definite proportions, **express the facts with perfect exactness.** The divergence between our experimental data and these laws we find to become smaller and smaller the more carefully our experiments are made. The difference between our best determinations and the ideal described by the law, is always less than the known errors of observation. There is, however, a second class of laws in which the opposite is the case. The more carefully our measurements are made, the more clearly is it recognized that the **second kind of law does not state the fact with exactness for any single example.** The known errors of measurement are in these cases less than the discrepancy between the observed fact and the ideal. The laws of Boyle, of Charles, and of Gay-Lussac are examples of this class. The value of such laws is not impaired by the fact that actual substances are in no case accurately described by them. The law gives us a norm of behavior to which most of the substances conform with a fair degree of closeness. Such a law resembles a limit in mathematics, toward which some expression tends to converge although it does not actually reach it. The first kind of law represents the actual behavior of materials, the second kind of law an average behavior to which no one material adheres with perfect exactness.

Now Avogadro's law belongs to the second class. No known gases conform to it with perfect strictness.

#### MOLECULAR WEIGHTS

**The Relative Weights of the Molecules.** — According to Avogadro's hypothesis, vessels of equal size filled with different gases contain equal numbers of gaseous molecules. Now equal volumes of different gases differ very markedly in weight, or, in other words, the densities of various known gases cover a wide range of values. Thus, hydrogen is the lightest of all, chlorine is more than thirty-five times, mercuric chloride (corrosive sublimate) vapor over one hundred and thirty-four times as heavy. Since these different weights of equal volumes represent the weights of equal numbers of molecules, the difference must be due to the differing weights of the

molecules themselves. The densities of gases, therefore, may be taken as measures of the relative weights of their individual molecules. The extreme significance of this inference in chemistry will appear as we elaborate upon it.

The various scales on which the densities \* of gases may be calculated, such as the weights of one liter of each gas, or the weights of volumes equal to that of one gram of air, are illustrated in the first two columns of the following table:

	Weight† of One Liter, 0° and 760 mm.	Density Air = 1.	Molecular Weight, Ox. = 32.
Hydrogen . . . . .	0.090	0.0696	2.016
Oxygen . . . . .	1.439	1.105	32.00
Chlorine . . . . .	3.166	2.449	70.92
Hydrogen chloride . . . . .	1.628	1.259	36.468
Carbon dioxide . . . . .	1.965	1.520	44.00
Water . . . . .	0.8045	0.622	18.016
Mercury . . . . .	8.957	6.908	200.6
Mercuric chloride . . . . .	12.121	9.354	271.52
Air . . . . .	1.293	1.00	28.955

The values for water (b.-p. 100°), mercury (b.-p. 357°), and mercuric chloride (b.-p. 305°) are measured at high temperatures and reduced by rule (p. 110) to 0° and 760 mm. All the numbers in the first two columns, as they stand, are purely physical in derivation. Those in the second column are obtained from those in the first by using the proportion:

$$1.293 \text{ (wt. 1 l. air) : 1.00 (air = 1) :: wt. of 1 l. any gas : } x$$

(where  $x$  = dens. of that gas on scale air = 1).

The last column will be explained presently. Since the numbers in the first column apply to equal volumes (1 l.), and those in the second stand in constant ratios to them, the weights in the second column represent equal volumes also. In the second, the volume is 1.175 l. The values in *either* one of the columns represent the

\* To speak strictly, the density of a gas is the weight of 1 c.c. at 0° and 760 mm. Its value for each gas is, therefore, obtained by dividing the numbers in the first column by 1000. The numbers thus obtained are, however, inconveniently small, and, besides, the beginner usually measures the weight of a liter of several gases in the laboratory, and so is more accustomed to the unit employed above.

† These are *not* the observed weights. The values have been corrected for the two deviations from the laws of gases (pp. 164-165).



relative weights of the molecules of the various substances (see Exercise 1 in this chapter).

In order to avoid the creation of unnecessary confusion in the mind of the beginner, the weights of one liter of gas in the above table are, with the exception of that of oxygen, all corrected for the deviations from the laws of Boyle and Charles (p. 164). This enables us to show the process by which the molecular weights are derived from the weights of one liter without the exhibition of arithmetical discrepancies which might obscure the principle being explained. The weights of one liter of the various gases, as we have given them, are based on the assumption that the molecules are always packed uniformly in accordance with Avogadro's hypothesis. The actual, measured values are in most cases somewhat different from these, and we attribute the divergencies to the varying degrees of cohesion between the molecules of different substances. Even the weight of one liter of the same gas, after reduction to 0° and 760 mm., is found to vary with the temperature and pressure at which it was examined. This is but natural, since changes in these conditions alter the effects of cohesion. The following table gives the *actual* weights of one liter of the same gases, with a few additional ones, and a comparison will show the extent of the divergencies. The most interesting case perhaps is that of oxygen and hydrogen. The chemical combining weights of these substances are in the ratio of 15.88 : 1.00, while a slight excess of cohesion in oxygen gives the ratio of their densities the value 15.90 : 1.00. These numbers are in both cases based upon Morley's results.

	Weight of One Liter, 0° and 760 mm.	Density, Air = 1.	Observed Molec- ular Weight, Ox. = 32.	Adjusted Molecular Weight.
Hydrogen . . . . .	0.08987	0.0695	2.01	2.016
Oxygen . . . . .	1.429	1.105	<b>32.00</b>	<b>32.00</b>
Nitrogen . . . . .	1.2507	0.967	28.02	28.02
Chlorine . . . . .	3.220	2.490	72.01	70.92
Hydrogen chloride . . . . .	1.6398	1.269	36.72	36.468
Carbon dioxide . . . . .	1.9768	1.529	44.28	44.00
Hydrogen sulphide . . . . .	1.537	1.189	34.43	34.976
Ammonia . . . . .	0.7708	0.597	17.27	17.034
Sulphur dioxide . . . . .	2.9266	2.264	65.56	64.06
Water . . . . .	0.8045	0.622	18.016	18.016
Mercury . . . . .	8.87	6.86	198.4	200.6
Air . . . . .	1.293	1.00	28.955	[Mixture]

**Molecular Weights.** — The foregoing section shows that, provided a substance is a gas or can be volatilized, the relative weight of its molecules, compared with those of other volatile substances, can be ascertained. To save words, the *relative weight of the molecule* of a substance is called the **molecular weight** of the substance.

Since the absolute weights of molecules cannot be accurately determined, the next question which arises is as to the choice of an appropriate unit, and therefore an appropriate scale for these relative weights, or molecular weights. Now the numbers already given, in the first two columns of the table, are purely physical data and, as they stand, lack direct relation to chemical facts. A set of *chemical* numbers is required for chemical purposes. We, therefore, proceed next to show how the required relation between the relative weights of molecules and chemical facts can be established.

Chemistry deals with chemical combination, and most substances are compounds. If we fix our attention, then, first, on compound substances and their molecules, we perceive at once that the molecules of a compound substance must contain two or more elements in definite proportions by weight. Thus the molecule of the compound will contain *one or more atoms of each of the component elements*. This conception at once suggests two ideas. In the first place, since we can now determine the relative weights of molecules, we should also somehow be able, with the help of the combining proportions, to determine the relative weights of the *atoms* of the elements. If these relative weights of atoms are properly determined, then the weights of the atoms, when added together, should give the weight of the molecule. Thus — and this is the second idea, and the one of most immediate use to us — the scale for relative weights of molecules must be chosen with reference to the scale for relative weights of the atoms, so that the former weights may always include the latter. That is to say, the molecular weights must be based upon the equivalent weights (p. 63). This means that the scale must be such that no molecule of a compound of hydrogen shall receive a value so small that the proportion of hydrogen in it is less than 1.008. Furthermore, since the atomic weight of oxygen is the standard for combining proportions, it is desirable to use this substance as basis of the scale of molecular weights. Now, as we shall find (see p. 240), it turns out that, to avoid obtaining proportions of hydrogen less than unity, we are compelled to take the scale 32 for the molecular weight of oxygen. Our *chemical* scale of densities is therefore calculated to the scale, **density of oxygen = 32**. This, then, is the answer to the problem with which the section opened. The third column of the table (p. 233) shows the results of re-calculating the densities to this chemical scale. The proportion used is:

Density of Ox. : Density of Substance :: 32 : x.

Thus, if we take the densities from the first column, the value for water is found by the proportion,  $1.429 : 0.8045 :: 32 : x$  ( $= 18.016$ ). That is, we multiply the weight of a liter of the gas by  $32/1.429$  to get the molecular weight.

Since the gram is the unit of weight, 32 g. of oxygen, or 18.016 g. of water is called the **gram-molecular weight** of the substance. It will be noted that 32 g. is not the weight of a molecule of oxygen. It is the weight of a very large number of molecules of oxygen (see p. 238). But, whatever that number of molecules of oxygen is, 18.016 g. of water contains the *same number* of molecules, and the other weights in the same column are weights of numbers of molecules equal to these. The term gram-molecular weight being somewhat ponderous, we abbreviate it to **molar weight**, and still further to **mole**. Thus, a *mole* of chlorine is 70.92 g. of the element, and a mole of hydrogen chloride is 36.468 g. of the compound.

When the above method of calculating the molecular weight from the weight of one liter of a substance is applied to the actual experimental values, the resulting molecular weights necessarily diverge somewhat from the ideal ones which we have given. Thus, since a liter of hydrogen chloride actually weighs 1.6398, this number when multiplied by 32 and divided by 1.429 gives the value 36.72. This is because the tendency to cohesion causes 1 liter of this gas to contain more molecules than does 1 liter of oxygen. The mole is always the adjusted molecular weight and not the observed one.

**The Gram-Molecular (Molar) Volume: G.M.V.** — The weights in the last column of the table (p. 233) must represent equal volumes of the different gases. This follows from the fact that they are derived from the values in the first column by multiplying by a constant ratio ( $32/1.429$ ), and the volume in the first column is always 1 liter. The actual dimension of this volume is evidently  $32/1.429$  liters, which is almost exactly 22.39, or in round numbers **22.4 liters**. This volume at  $0^\circ$  and 760 mm. holds 32 g. of oxygen, 70.92 g. of chlorine, 44.00 g. of carbon dioxide, or, in fact, the molar weight of any gaseous substance. It is called, therefore, the **gram-molecular volume (G.M.V.)** or the **molar volume**. It may be defined as **that volume which contains one mole (gram-molecular weight) of any gas at  $0^\circ$  and 760 mm.** At other temperatures and pressures the G.M.V. has correspondingly different volumes.

The G.M.V. gives us a concrete conception of a molar weight. This volume is represented by a cubical wooden box (Fig. 93) 28.19 cm. (or about 11.1 inches) high. Like any other volume, it holds

identical numbers of molecules of different gases.\* Its capacity at  $0^{\circ}$  and 760 mm. is the number of molecules in 32 g. of oxygen. Hence, in terms of molecules, the weight of any gas which fills it bears to 32 g. the same ratio as the weight of a molecule of that gas to the weight of a molecule of oxygen.

### *Measurement of Molar Weights (Moles).*

— We may now state the method of finding the molar (gram-molecular) weight of a substance thus: Weigh a known volume of the substance, at any temperature and pressure at which it is gaseous, reduce this volume by rule to  $0^{\circ}$  and 760 mm., and calculate by proportion the weight of 22.4 liters (see Exercises 1, 2, 3, 4).

That quantity of each substance, simple or compound, which at  $0^{\circ}$  and 760 mm. would fill the G.M.V. cube is the unit quantity of the substance for all theoretical purposes in chemistry. It represents the relative weight of the molecules of the substance. We shall employ it at once for the purpose of determining the *relative weights of atoms*, or atomic weights.

It is evident that the chemical molecular weights, adjusted so as to include whole numbers of equivalent weights, will not all occupy exactly equal volumes. They represent exactly equal numbers of molecules, and the slight differences in the closeness with which the molecules are packed (p. 234) will cause the values of the molar volumes to differ from gas to gas. The values of the volume actually containing equal numbers of molecules are as follows: Hydrogen, 22.40; oxygen, 22.39; nitrogen, 22.45; chlorine, 22.01; hydrogen chloride, 22.23; carbon dioxide, 22.26; water, 22.39; mercury, 22.55. The average value of this volume in the case of the more nearly perfect gases is 22.4 liters, and this is, therefore, the number which we have used in our definition.

\* A common question is: Do not molecules of different substances differ in size, and will not the numbers required to fill the G.M.V. therefore be different? The answer is that the molecules are all so small compared with the spaces between them (at 760 mm.) that the distances from surface to surface are practically the same as from center to center. A G.M.V. of oxygen, when liquefied, gives less than 32 c.c. of liquid oxygen, or less than  $1/700$  of the volume as gas. It is only when gases are so severely compressed that the nearness of the molecules to one another approaches that found in the liquid condition that the effects of the bulk of the molecules become conspicuous, and a difference in the behavior of different gases becomes noticeable. But in the kind of chemical work discussed in this chapter, pressures over one atmosphere are not used.

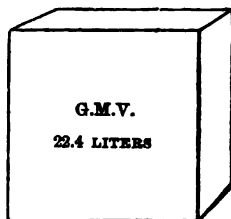


FIG. 33.

***The Number of Molecules in a Mole or in 22.4 Liters.***—

The molecular weight or mole of a substance is not the weight of a single molecule. It is only the *relative* weight of the molecule of the substance. It is, however, the weight in grams of a fixed number of molecules, for 22.4 liters (or any other volume) contains equal numbers of molecules of different gases. The actual number has been determined. Thus Jean Perrin found values by several experimental methods which ranged between  $5.9 \times 10^{23}$  (that is, 59 followed by 22 ciphers) and  $6.9 \times 10^{23}$ . Rutherford, using an entirely different plan, obtained  $5.7 \times 10^{23}$  for the gas helium. This value was obtained by observing that 0.46 cubic millimeters of helium ( $0^\circ$  and 760 mm.) were given off by 1 gram of radium (*q.v.*) every 24 hours. Now the molecules of helium, when they strike a screen covered with zinc sulphide, produce flashes of light. By counting the flashes appearing in a certain restricted area in one minute, and multiplying by the proper factor, to get the total number emitted on all sides during that time, and further multiplying by 1440 minutes (= 24 hours), the number of molecules filling 0.46 c. mm. was obtained. From the result, the numbers in 1 c.c. and in 22.4 l. were calculated. The value at present accepted as most accurate is that obtained by R. A. Millikan of the University of Chicago, by the use of a still different method, namely  $6.07 \times 10^{23}$  (or  $6070_{21}$ ).

Accepting one of these values, *e.g.*, that of Millikan, we can evidently calculate the weight of a single molecule of any gaseous or volatile substance. Thus, a single molecule of oxygen must weigh  $32/6.07 \times 10^{23}$  g., or  $5.3 \times 10^{-23}$ , or  $0.0_{2553}$  g.

***The Chemical Molecule.***—It will be noted that we get definite, quantitative information about individual molecules by the study of gases. We shall find, later, that we can also obtain similar information about molecules of substances in dilute solutions, because, in that condition, the molecules are separated from one another and scattered throughout a considerable space, much as they are in gases (p. 184). **Chemical molecules are the units of which gases, and bodies in dilute solution, are aggregates.** We have means of comparing, roughly, at least, the dimensions of the physical units in gases and liquids, and find that in the liquid state the molecules are often multiples of the gaseous ones (*cf.* water, p. 202). The gaseous molecules are, therefore, our standard in chemistry.

Many authors discuss the breaking up of a solid, like salt or glass, until particles are obtained which cannot be further split. They use this in the

attempt to make clear that there is a limit to pulverization, reached when the material has been reduced to single molecules. Now, this process is purely imaginary, and cannot actually be carried out. Chemistry is an experimental science, and only the *real* experiments which lead to a given result should be described. This statement about pulverization is disingenuous, to say the least, for there are no facts behind it. Aside from that objection, no conditions are usually stated that would prevent one from dividing the molecules into atoms, and the atoms into electrons and positively charged nuclei (see Chap. XXII). Since the process is usually stated to be imaginary, there is no particle so small but that one can *imagine* it being split into two, or even twenty parts, and there is thus no way of stopping the imaginary splitting at the right point. An active imagination could split salt into small fractions of electrons, although we have no experimental knowledge of the existence of such fragments. The imagination is of great value in suggesting possibilities, to be tested experimentally, but it cannot be used, alone, for ascertaining facts, and it is crime against the spirit of true science to suggest the contrary to a naturally confiding reader.

### ATOMIC WEIGHTS

#### ***Determination of the Atomic Weight of Each Element. —***

If the paragraphs dealing with combining weights are now re-read (pp. 61-63), it will be found that the foundations for a system of weights was worked out, but that no basis for *definitely fixing* the individual values was discovered. At the time, the only information we had was obtained by analyzing compounds and reasoning about the results, and evidently something more was needed for the absolute determination of the values. Thus on p. 66, it is pointed out that the equivalent weight, or *any multiple of it by an integer*, will serve for expressing the proportions used by the element in combining with other elements. We are now approaching the question of units, in which to express combining proportions, *from a different viewpoint*. We were then assigning numbers for the quantities of the constituent elements of a compound (such as iron : oxygen :: 111.68 : 48, p. 13) **without any consideration of the magnitude of the total weight of the constituents**. At that time, we had no reason before us to indicate that this total might require consideration. **We now start by determining and assigning the total weight of the compound**, and it is our next task to consider the **subdivision of this total amongst the constituents**. Evidently, if the unit quantity of the compound has been properly chosen, it must be sub-divisible into one or more unit quantities, of suitable dimensions, of each element in the compound.

To determine the atomic weights, the plan of procedure is perfectly simple. In the preceding section we settled upon the chemical unit quantity of each *substance*. This is the quantity which, in the gaseous condition, would fill the G.M.V. (22.4 liters) at 0° and 760 mm. Now, we seek the chemical unit quantities of the *elements* combined in each substance. Evidently the logical and consistent plan must be to take the amount of each substance which fills the G.M.V. and find out how much of each element present is contained in this unit amount of the substance. In other words, to put the matter concretely, we imagine ourselves filling the cube (Fig. 93) with one compound after another, and in each case determining by analysis the weight of each constituent element present in a cube-full of the substance. To carry out this plan, two experimental operations are necessary with each substance:

First we determine the density, and this gives us the gram-molecular weight, *i.e.*, the amount filling the cube. This shows the relative weight of a molecule of the substance, as compared with that of one molecule of oxygen.

Second we analyze the substance, and this gives us the quantity of each constituent in the total gram-molecular weight, *i.e.*, in the material filling the cube. This, in turn, shows the weight of the quantity of each element present in each molecule, relative to the weight of a molecule of oxygen.

For example, the cube holds 36.468 g. of hydrogen chloride, and this amount, when decomposed, yields 1.008 g.\* of hydrogen and 35.46 g. of chlorine.

Finally, to determine the best unit weight for a given element, we repeat the two foregoing operations with as many different compounds of the element as possible, and then we examine the various quantities of the element found in the G.M.V. of the various compounds. From inspection of these quantities we quickly select the value of which all are multiples, by unity or some integral number. This value for the unit weight is the one accepted as the atomic weight. This is the weight of one atom of the element, compared with the weight of a molecule of oxygen, and molecules containing

\* It will be observed that if the unit for molecular weights had been less than the number of molecules in 32 g. of oxygen, then an equal number of molecules of hydrogen chloride would have contained less than 1.008 g. of hydrogen, and the atomic weight of this element would then have been less than unity. Theoretically, any value for hydrogen would serve the purpose, but there are arithmetical conveniences in having one value in the list close to unity.

more than this proportion contain two, three, or more atoms of the element.

For example, if we are seeking the atomic weight of chlorine, we set down the result for hydrogen chloride just given. Then we take another compound of chlorine, say phosphorus oxychloride (a liquid). We determine the weight of a measured volume of its vapor, at a properly chosen temperature and pressure, and the result gives us, by calculation, the molecular weight, *viz.* 153.38. That is, 153.38 g. of the substance would fill the cube, if it could be kept as vapor at 0° and 760 mm. And this amount of the substance contains 31 g. of the element phosphorus, 16 g. of the element oxygen, and 106.38 g. of the element chlorine. We then continue the processes described, using all the volatile compounds of chlorine. The involatile compounds (like common salt) must be set aside, for they cannot be vaporized, and therefore their molecular weights cannot be determined. When we have studied as many compounds as possible in this way, we find that there are different quantities of chlorine in our list, *but they are all integral multiples of 35.46 g.* In phosphorus

Substance.	Molar Weight.	Weights of Constituents in Molar Weight.						Molecular Formula.
		Hydrogen.	Chlorine.	Oxygen.	Phosphorus.	Carbon.	Mercury.	
Hydrogen chloride . . . . .	36.46	1	35.46	...	...	...	...	HCl
Chlorine dioxide . . . . .	67.46	...	35.46	32	...	...	...	ClO <sub>2</sub>
Phosphorus trichloride . . . . .	137.38	...	106.38	...	31	...	...	PCl <sub>3</sub>
Phosphorus oxychloride . . . . .	153.38	...	106.38	16	31	...	...	POCl <sub>3</sub>
Phosphoric anhydride . . . . .	284	...	...	160	124	...	...	P <sub>2</sub> O <sub>10</sub>
Phosphine . . . . .	34	3	...	...	31	...	...	PH <sub>3</sub>
Water . . . . .	18	2	...	16	...	...	...	H <sub>2</sub> O
Methane . . . . .	16	4	...	...	...	12	...	CH <sub>4</sub>
Acetylene . . . . .	26	2	...	...	...	24	...	C <sub>2</sub> H <sub>2</sub>
Propane . . . . .	44	8	...	...	...	36	...	C <sub>3</sub> H <sub>8</sub>
Formaldehyde . . . . .	30	2	...	16	...	12	...	CH <sub>2</sub> O
Acetic acid . . . . .	60	4	...	32	...	24	...	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>
Mercurous chloride . . . . .	235.46	...	35.46	...	...	...	200	HgCl
Mercuric chloride . . . . .	270.92	...	70.92	...	...	...	200	HgCl <sub>2</sub>

oxychloride, for example, the quantity was 106.38, or  $3 \times 35.46$ . Hence 35.46 g. can be taken as the unit quantity, the **atomic weight** of the element chlorine. This is the relative weight of an atom of



chlorine, as compared with the weight of a molecule of oxygen, when the value 32 is assigned to the latter.\*

In the preceding table a few sample results of the process just outlined are given. The first column contains the molar weight, *i.e.*, the weight of the substance which occupies the G.M.V. cube. In the other columns are entered the weights of the various elements which together make up the total molar weight. To simplify the numbers, the value of 1 is used for hydrogen, instead of 1.008.

To contain similar data for all the volatile compounds of every known element, a huge table, of which this might be a small corner, would be required. With such a table at hand the atomic weight of each element could promptly be picked out. Thus, in the carbon column it would be found that all the weights of carbon were either 12 or integral multiples of 12, and this is therefore the atomic weight of carbon. Similarly the atomic weight of oxygen is 16,† of phosphorus 31, of mercury 200 (see Exercise 4).

When the atomic weights have finally been selected, we can go through the table and change all the numbers into multiples of the chosen atomic weights. Thus, for 70.92 we write  $2 \times 35.46$ , and for 106.38 we write  $3 \times 35.46$ , and so forth. The reader should prepare such a modification of the table. With this new form of the table before us, we can, finally, replace the atomic weights by the symbols which stand for them, writing, for 35.46, Cl, for  $2 \times 35.46$ ,  $\text{Cl}_2$ , and so forth. The results of doing this in each line, *i.e.*, for each substance, are collected at the ends of the lines in the last column of the table. The reader should himself repeat the substitutions of the symbols, and so verify the formulæ given. These formulæ, since they are based on the molecular weights, in such a way that when the numerical values are substituted for the symbols the total restores to us the molecular weight, are called **molecular formulæ**.

The mode of derivation makes all the quantities of any one element in the above table integral multiples of the smallest. Of course, an element might be found of which no volatile compound

\* It should be noted that there is another unit quantity of chlorine, namely the molecular weight, or weight of the G.M.V. of the *substance*. This is the unit quantity of free chlorine. But we are dealing now with compounds, and proportions in combination, so that free, uncombined chlorine, and other elements in free condition do not interest us at present, and will be taken up later.

† The difference between the unit quantity of oxygen in compounds (namely, 16) and the unity quantity of free oxygen (32) will be discussed presently.

containing the unit weight was yet known. If methane and formaldehyde were still undiscovered, and only the other three compounds containing carbon were available, we should then take the greatest common measure of 24 and 36, namely 12, as the unit.

**The chemical unit weight or atomic weight of an element** may thus be defined as: The G.C.M. (greatest common measure) of the weights of that element found in the molar weights of all its volatile compounds so far as these have been examined.

**Atomic Weights and Equivalent.** — It will now be seen why the equivalents (p. 63) were multiplied by various integers in making the chemical units. The equivalent of carbon was 3. That is to say, carbon and oxygen combine in the ratio 3 : 8 (in carbon dioxide), and carbon and hydrogen in the ratio 3 : 1.008 (in methane). But there is no compound of carbon whose molecular weight contains less than 12 parts of the element. It would thus lead to needless complication to take 3 as the unit amount of carbon, for every molecule would then contain four units, or some multiple of four, and every formula  $C_4$  or some multiple of  $C_4$ . We choose the largest units of combining weight that we can, in order that the coefficients may be the smallest possible, and the resulting formulæ the simplest possible. Naturally the actual ratios remain the same. Thus, for carbon dioxide the ratio 3 : 8 is replaced by 12 : 32, or 12 :  $2 \times 16$ , or C : 2O, which has the same value.

Since the atomic weight is thus always a multiple of the equivalent weight (by unity, or some other integer), it might also be defined as: **The largest integral multiple of the equivalent which can be contained in the molecular weights of all the volatile compounds of the element.** The complete list of accepted atomic weights is printed on the inside of the cover at the back of this book.

The conclusion that  $C = 12$  is the most convenient value is reached also by studying the chemical interactions of carbon compounds. If the symbol  $C$  stood for three parts (the equivalent) of carbon, methane would receive the formula  $CH$ , the proportion of its constituents by weight being 3 of carbon and 1 of hydrogen. But, when we mix this gas with chlorine and expose the mixture to sunlight, no less than four different compounds are produced (cf. p. 225). With  $C = 3$ , their formulæ would be  $C_4H_3Cl$ ,  $C_2HCl$ ,  $C_4HCl_3$ , and  $CCl$ , the carbon being univalent. The relations of these substances are much simplified when we change to molecular formulæ and substitute  $C = 12$  for  $C_4 = 12$ , making the carbon quadrivalent.

We then perceive that we are displacing successively the four hydrogen units in one molecule, and that the substances are  $\text{CH}_4$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$ . The whole prodigious growth of the chemistry of the compounds of carbon, which has taken place during the last half century, has been the result of the employment of this seemingly slight improvement by Gerhardt and Laurent, and by Williamson, and its enforcement and extension by Kekulé and Couper, independently of one another, in 1858. Thus, quite aside from the molecular theory and Avogadro's addition to it, we have now found ample independent justification for the multiplication of the equivalents by integers and for the conception of valence which results from this.

**Further Comments on Atomic Weights.**—The fact that *all* the numbers in any one column of the table (p. 241), turn out to be even multiples of a single number need not seem mysterious. The molecule of every compound containing chlorine must contain one, two, three, or some other *whole* number of chlorine atoms, for chlorine atoms, like other atoms, do not furnish fractions of atoms in any cases of combination. Now, the weight of chlorine in 6070<sub>21</sub> atoms, assuming one atom of chlorine to each molecule in 22.4 liters, must be 35.46 g. Hence, if the weight of chlorine in 22.4 liters (6070<sub>21</sub> molecules) of the compound differs from 35.46 g., it can do so only because there are two atoms of chlorine per molecule, giving  $2 \times 35.46$  g., or three atoms giving  $3 \times 35.46$  g. of chlorine, and so forth. Thus the quantities of chlorine in the G.M.V. of *all* compounds of chlorine must be multiples of 35.46 by unity or some other integer.

It is hardly necessary to add that the atomic weights, found as described above, are equally serviceable in expressing the compositions of compounds which are *not* volatile. The atoms in non-volatile compounds are identical in properties with the atoms of the same elements in volatile compounds. If an element gives no volatile compounds, other methods of fixing its atomic weight are available (see Dulong and Petit's law, p. 245).

Although in this section, as well as elsewhere, we have emphasized the fact that atoms are not divided into parts, this must not be taken to mean that atoms are incapable of being broken up. It means only that in ordinary chemical changes, the atoms combine and separate as wholes. Indeed, we now know that the atom of radium (*q.v.*) gives off atoms of helium, and leaves an atom of lead,

and that the atoms of one or two other elements *disintegrate* in a similar way. Some day means of breaking up any or all kinds of atoms may be discovered.

**Advantages of Atomic Weights.**—Although the method of selecting atomic weights involves rather complex reasoning, these weights repay the trouble, because they represent the relative weights of the atoms themselves. They are thus much more valuable in helping us to understand chemical behavior and in enabling us to classify the phenomena of chemistry than would be any other units of weight we might have chosen. The following are some of the advantages they offer:

1. The atomic weight of an element has but one value, and this value is definitely determinable.

2. The atomic weight of an element has a valence (p. 130), while equivalents are equi-valent. While valence is a helpful conception in all branches of chemistry, organic chemistry is especially indebted to the conception of the quadrivalence of carbon for much of its development and most of its organization. The full illustration of this point is beyond the limits of the present book.

3. The periodic system (*q.v.*), the basis of a plan for classifying the properties of all chemical substances, is founded upon the atomic weights.

4. Dulong and Petit's law is based upon atomic weights. This law furnishes also an alternative means of determining atomic weights that has frequently rendered valuable service, and on this account forms the subject of the next section.

**Dulong and Petit's Law, an Alternative Means of Determining Atomic Weights.**—It was first pointed out (1818) by Dulong and Petit, of the École Polytechnique in Paris, that when the atomic weights of the elements were multiplied by the specific heats of the simple substances in the solid condition, the products were approximately the same in all cases. In other words, the specific heats are inversely proportional to the magnitudes of the atomic weights. The table, in which round numbers have been used for the atomic weights, shows that the product lies usually between 6 and 7, averaging about 6.4:

Element.	Atomic Wt.	Sp. Ht.	Prod-uct.	Element.	Atomic Wt.	Sp. Ht.	Prod-uct.
Lithium . .	7	.94	6.6	Iron . . . . .	56	.112	6.3
Sodium . .	23	.29	6.7	Zinc . . . . .	65.4	.093	6.1
Magnesium .	24.3	.245	6.0	Bromine (Solid)	80	.084	6.7
Silicon . . .	28.3	.16	4.5	Gold . . . . .	197	.032	6.3
Phosphorus (Yellow)	31	.19	5.9	Mercury (Solid)	200	.0335	6.7
Calcium . .	40	.170	6.8	Uranium . .	238	.0276	6.6

Another way of expressing this law will give it greater chemical significance. The specific heats are the amounts of heat required to raise one gram, that is one *physical* unit, of each element through one degree. When we multiply this by the atomic weight, we obtain the amount of heat required to raise one gram-atomic weight of the element, that is, one chemical unit, through one degree. The values of this product are approximately equal. Since there are equal numbers of atoms in one gram-atomic weight of each element, it follows that: **Equal amounts of heat raise equal numbers of atoms of all elements in the solid form through equal intervals of temperature.**

The conspicuous exceptions occur among the elements with low atomic weights only. The products for four of these, the atomic weights being given in parentheses, are as follows: Glucinum (9), 3.7; boron (11), 2.8; carbon (12), 1.7; and silicon (28.4), 4.5. Further investigation shows, however, that in the case of precisely these elements the value found for the specific heat varies very markedly with the temperature at which the specific heat is measured. Their specific heats become rapidly greater the higher the temperature. Thus at 985° the specific heat of the diamond (carbon) is 0.45, which when multiplied by the atomic weight gives the product 5.5. So that even the exceptional elements tend to come into line when the specific heat is measured at higher temperatures — and Dulong and Petit's statement does not limit our choice to any one temperature.

It will be seen at once that although the law of Dulong and Petit is purely empirical, it may nevertheless be used for **fixing the atomic weight of an element of which no volatile compounds are known.** We can always measure the equivalent with considerable exactness, and, when this has been multiplied by the specific heat of the free substance, we can see at a glance what integral factor will raise the product to the neighborhood of 6.4. For example, analysis shows us that in calcium chloride the proportion of chlorine to calcium, using the known atomic weight of chlorine as one term of the proportion, is 35.46 : 20. If calcium is univalent, 20 is its atomic weight. If it

is bivalent, two units of chlorine are combined with 40 parts of calcium, and 40 is its atomic weight. If it is trivalent, three units of chlorine are united with 60 parts of calcium, etc. All we learn in reference to the atomic weight of calcium from this analysis is that its value is 20 or some integral multiple of 20. Nor can we fix the upper limit, for we are unable to obtain the weight of a known volume of calcium chloride vapor and so determine the molecular weight. But the specific heat of solid calcium being 0.170, we multiply this number by 20, and get the product 3.4. This is only half large enough, so we find that 40 is the value for the atomic weight of calcium. The product is then 6.8, which agrees fairly well with the average for other elements. We decide, therefore, that the symbol Ca shall represent forty parts by weight. The formula of calcium chloride is therefore  $\text{CaCl}_2$ , and calcium is bivalent.

It will be seen that this does not supply us with a method of ascertaining chemical unit weights independently of any chemical experiment. We cannot measure the specific heat and use the quotient from division of this number into 6.4, for we do not know in advance that the product for the element will have exactly this value. It may be below 6, or it may be as high as 7. In the case of calcium, for example,  $6.4 \div 0.17 = 37.65$ . Now 37.65 is 5 per cent below the real value of the chemical unit, and even the roughest measurement of a chemical combining weight need never be more than 1 per cent in error. Hence the atomic weight must be founded upon the determination of the equivalent, which can be measured with accuracy. The rule discussed in this section can be used only to ascertain what multiple of the equivalent shall be accepted as the atomic weight after the equivalent itself has been measured with care. In other words, this is a method of adjusting the result of chemical experimentation, and cannot supersede it altogether.

The existence of the law of Dulong and Petit and the periodic law, together with the services of structural formulæ to organic chemistry, all demonstrate that atomic weights are of vastly greater significance in the science than are equivalent weights. And there are other immense ranges of facts, aside from those covered by these conceptions, which are all dependent upon the atomic weights. That almost the whole systematization that has been secured in chemistry should thus center in this one point, furnishes the strongest circumstantial evidence that Avogadro's law is in accord with the facts. This independent inductive evidence in favor of Avogadro's principle is especially worth noting because the deduction of the principle from the data of the kinetic-molecular theory is not absolutely rigid. It involves certain assumptions which, while they are plausible enough, are still assumptions.

**Historical.** — The idea that matter is composed of small particles is a very ancient one. Not even Dalton (1805), however,

although he used this conception continually as a means of thought about chemical and physical phenomena, made any distinction between atoms and molecules. This distinction was introduced later by Avogadro (1811). Yet, without this refinement, continual thought of the behavior of matter as consisting in transactions between small particles led Dalton to see that it was probable that individual unit weights for each element must exist. The discovery that they did exist soon followed. The numbers which Dalton actually gave out, aside from the considerable experimental inaccuracies attached to them, were often equivalents and not modern atomic weights. It was after the publication of Dalton's ideas that Gay-Lussac discovered the law of combining volumes (1808), and until this law was discovered there was no criterion for fixing the values of the atomic weights. Gay-Lussac, at the end of his paper, pointed out that his discovery formed an important confirmation of Dalton's views. Strange to say, Dalton himself refused to accept Gay-Lussac's law, and so rejected the very means by which his own principle of chemical unit weights came eventually to be acknowledged as one of the foundation stones of the science. On the other hand, Dalton's fellow countrymen and contemporaries accepted the principle of unit weights, but rejected the atomic hypothesis by the help of which Dalton had reached them! Thus Sir Humphry Davy called them "proportions" instead of atomic weights, and Wollaston preferred the word "equivalents."

Gerhardt and Laurent, and Williamson used Avogadro's law long before 1858, and employed correct atomic weights, so far as the elements possessed volatile compounds. But there was much difference of opinion about the best atomic weights for the other elements, and some difference even in regard to elements like oxygen. Thus, many still wrote the formula of water  $\text{HO}$ , where  $\text{O} = 8$ . It was only after Cannizzaro (1858) demonstrated the value of Dulong and Petit's law (discovered forty years before) for settling the atomic weights of elements, like calcium and iron, which gave no easily volatile compounds, that rapid progress towards complete agreement was made.

Many chemists have contributed to the determination and revision of the atomic weights. The Swedish chemist, Berzelius, devoted many years to the accurate measurement of combining proportions. Stas, a Belgian (1860-1870), made a number of determinations with great exactness. Morley's (1895) value for combining proportions of hydrogen and oxygen alone represented twelve years of

work. T. W. Richards of Harvard University has carried many of the values to a higher degree of accuracy.

### MOLECULAR FORMULÆ

**Molecular Formulæ of Compounds.** — If the molar formulæ in the table (p. 241) be examined it will be observed that several are not in their simplest terms. Thus, the formula of acetylene is  $C_2H_2$ . The formula  $CH$  would represent the composition of the substance equally well, for 12 : 1 is the same as 24 : 2. But the formula  $CH$  gives a total of only 13, while  $C_2H_2$  shows the total weight of the molecule to be 26 and records for us therefore *the weight of the G.M.V.*, as well as the composition of the substance. We shall find this additional property, peculiar to the molecular formula, to be a feature of the greatest practical value. Some of the practical uses of this improvement in our formulæ will be illustrated in this chapter, and there is an example of one of them in the table itself. Thus, the molecular formula of acetic acid is  $C_2H_4O_2$ , and not the simpler, identical proportion  $CH_2O$ . The latter is the molecular formula of a totally different substance, formaldehyde, now much used as a disinfectant. The vapor of this substance has only half the density of acetic acid vapor, and this fact, recorded in the formula, helps to remind us that the substances are different. Still another substance of the same composition is grape sugar (dextrose),  $C_6H_{12}O_6$ . In addition to this and other practical advantages, molecular formulæ satisfy also the claim of logical consistence. If the symbols represent the atomic weights, the formulæ should be constructed so as to represent the molecular weights.

Molecular formulæ like  $C_2H_2$  and  $C_2H_4O_2$  are easily interpreted in terms of the atomic hypothesis. C represents one atom of carbon, and H one atom of hydrogen. But there is no reason why a molecule of acetylene should not contain two atoms of each kind. Similarly, the molecule of formaldehyde contains four atoms ( $CH_2O$ ), and one of acetic acid eight atoms ( $C_2H_4O_2$ ), and one of dextrose twenty-four atoms ( $C_6H_{12}O_6$ ), although the relative numbers of each kind are the same. Indeed, this hypothesis helps to clear the matter up, for chemists go so far as to account for the chemical behavior of the substances by an imagined geometrical arrangement of the atoms in their molecules, and these three kinds of molecules are supposed to differ in structure as well as in the number of atoms they contain.



**The Molecular Weights and Formulæ of Elementary Substances.**—The following table gives the densities of some elementary substances, including those of which the substances last discussed are compounds. The first column shows the atomic weight, which in each case is the minimum weight of the element found in a G.M.V. of any compound. For example, 16 g. of oxygen

	Atomic Weight.	Sym- bol.	Density, O = 32.	Density Fac- torized.	Formula of Free Element.
Oxygen . . . . .	16.00	O	32.00	$2 \times 16.00$	O <sub>2</sub>
Hydrogen . . . . .	1.008	H	2.016	$2 \times 1.008$	H <sub>2</sub>
Chlorine . . . . .	35.46	Cl	70.92	$2 \times 35.46$	Cl <sub>2</sub>
Phosphorus . . . . .	31.0	P	124.0	$4 \times 31.0$	P <sub>4</sub>
Mercury . . . . .	200.6	Hg	200.6	$1 \times 200.6$	Hg
Ozone . . . . .	16.00	O	48.00	$3 \times 16.00$	O <sub>3</sub>
Cadmium . . . . .	112.4	Cd	112.4	$1 \times 112.4$	Cd
Potassium . . . . .	39.10	K	39.10	$1 \times 39.10$	K
Sodium . . . . .	23.00	Na	23.00	$1 \times 23.00$	Na
Zinc . . . . .	65.37	Zn	65.37	$1 \times 65.37$	Zn

and 35.46 g. of chlorine are the weights in the amounts of water vapor and hydrogen chloride, respectively, which fill the cube (22.4 liters). The symbol, in the next column, stands for this quantity and occurs in many formulæ, such as H<sub>2</sub>O and HCl. It represents the combining unit or atom. In the third column is given the density of the free, elementary substance. This number of grams of the simple substance fills the G.M.V. and this number is the molecular weight. It shows the weight of the molecule relative to the weights of the other molecules in the same column, and to the weights of the atoms in the first column. In the last two columns are given the densities resolved into multiples of the atomic weights and the corresponding formulæ.

The reader cannot fail to note a striking peculiarity. In the case of chlorine the molecular weight is 70.92, while the atomic weight is 35.46. With hydrogen and oxygen, also, the molecular weight contains two atomic weights. Yet this is not a general rule, for with mercury and several other elements the molecular and atomic weights are alike, while with phosphorus the molecular is four times the atomic weight. Evidently there is no rule, and each element has to be subjected to separate experimental study. The result is that for *free, elementary chlorine we use the molecular formula Cl<sub>2</sub>*, for *free hydrogen H<sub>2</sub>*, for *elementary, uncombined oxygen the formula O<sub>2</sub>*. For

a substance like phosphorus, which is not a gas and is not often measured as a vapor, the formula  $P$  is commonly employed by chemists, to avoid the larger coefficients which  $P_4$  introduces into equations, although theoretically the latter formula would be the strictly correct one.

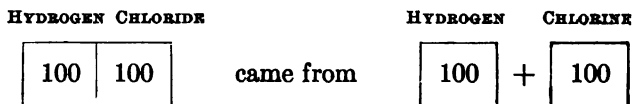
The case of oxygen demonstrates clearly the necessity of using molecular formulæ, even for simple substances. The table shows *two* substances containing nothing but oxygen. Ozone (*q.v.*) has a molecular weight 48, being a gas exactly one-half heavier than ordinary oxygen. Its formula, therefore, is  $O_3$ , while that of oxygen is  $O_2$ . Oxygen and ozone are entirely different chemical individuals. The latter has, for example, a strong odor and is much more active. Thus polished silver remains bright indefinitely in pure oxygen, but oxidizes quickly when placed in ozone.

To avoid a common error, the reader should note that to learn the *atomic* weight of an element, we do *not* measure the molecular weight of the *simple* substance. The molecular weight of the elementary substance may be a multiple of the atomic weight, and we find out whether it is such a multiple only after the atomic weight has been determined. The atomic weight is the unit weight *used in compounds*, and can be ascertained only by a study of compounds. The molecular weight of the free element gives us only a value which we know must be a multiple of the atomic weight, by 1 or some other integer.  $\text{Mol. Wt.} = \text{At. Wt.} \times x$ , where  $x$  is 1 or some other integer.

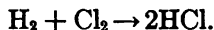
**Further Discussion of the Molecular Formulæ of Elementary Substances.** — Some further explanation may be required, to the end that the reader may be reconciled to accepting the formulæ  $Cl_2$ ,  $O_2$ , and so forth. In the first place, he should note how these formulæ arose. If we accept Avogadro's law, and the inference from it to the effect that the weights of equal volumes of gases are in the same ratio as the weights of their individual molecules, then we cannot escape the conclusion to which measuring the relative densities of free chlorine and hydrogen chloride, for example, leads. The ratio of their densities is 70.92 : 36.46. That is to say, the relative weights of a molecule of chlorine and a molecule of hydrogen chloride stand in this ratio. The molecule of chlorine is nearly twice as heavy as the molecule of the compound, *and there cannot therefore be a whole molecule of chlorine in a molecule of hydrogen chloride.* In fact, we perceive at once that the molecule of hydrogen chloride

must contain only half a molecule of chlorine (35.46), together with half a molecule of hydrogen (1). In other words, if the molecule of free chlorine were to be taken as the atom of the element, then the molecule of hydrogen chloride would contain only half an atom of chlorine, which would be contrary to our decision to take as atoms quantities which are not divided. So we choose the other horn of the dilemma, and say that the specimen of chlorine in the molecule of hydrogen chloride is a whole atom and that therefore the amount of chlorine in the molecule of free chlorine is two atoms, and its formula  $\text{Cl}_2$ . Similarly, the weight of hydrogen in the molecule of hydrogen chloride is 1.008, while that of the molecule of hydrogen is 2.016, so that there are two atoms in the molecule of free hydrogen and its formula is  $\text{H}_2$ . Reasoning in like manner from the molecular weights of oxygen (32) and water (18) we reach the conclusion that the molecule of oxygen is **diatomic** ( $\text{O}_2$ ).

Still another way of looking at the same facts may shed light on the matter. When hydrogen and chlorine combine, one volume of each of these gases gives two volumes of hydrogen chloride (p. 228). Let us imagine the experiment to be made with minute volumes holding one hundred molecules each:

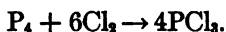


The 200 molecules of hydrogen chloride must contain at least 200 fragments of chlorine, since there is a sample in each molecule. Now the 200 fragments of chlorine came from a volume containing only 100 *molecules* of chlorine. Each of the latter must therefore have been split in the chemical action. Hence the molecules of free chlorine contain at least two atoms. Parallel reasoning leads to the conclusion that the molecules of free hydrogen are likewise diatomic. If we consider the molecular formula of a substance as representing one molecule (see below), the equation for this action is:



There are two molecules on each side of the equation, and this corresponds with the fact that there is no change in the total volume. Again, we find that one volume of oxygen furnishes enough of the element for two volumes of water vapor (p. 156). We infer therefore that each molecule of oxygen is divided into two parts in the

action. And in like manner, when we find that one volume of phosphorus vapor, in combination with six volumes of chlorine, gives *four* volumes of phosphorus trichloride vapor, we infer that every molecule of phosphorus furnished enough of the element for four molecules of phosphorus trichloride, and contained therefore four atoms (see Exercise 3, p. 265).



The simple fact that hydrogen and oxygen, when mixed, do not combine (p. 126) may assist in reconciling us to the diatomic nature of their molecules. Some part of the mixture has to be heated strongly to start the interaction. Now the molecular formulæ,  $\text{H}_2$  and  $\text{O}_2$ , suggest that each gas is really in combination already (with itself), and they therefore explain to some extent the indifference of the gases towards one another. If the molecules were free atoms, they could not encounter one another continually as they move about, and yet escape combination as we observe that they do. We may imagine that the primary effect of heating is to decompose some of the molecules, and liberate hydrogen and oxygen in the atomic condition, and that the combination of these atoms starts the explosion of the whole mass.

In the case of hydrogen, the diatomic nature of the molecules has been demonstrated by an entirely different method by Irving Langmuir. It has long been known that the conductivity of hydrogen for heat is greater than that of any other elementary gas. Thus, a wire raised to a white heat in air by means of an electric current cannot be kept at a red heat, even, by the same current in hydrogen. In other gases, heat from the hot wire is used up in accelerating the motion of the molecules of the gas. Langmuir has shown, however, that in hydrogen, additional heat is consumed in causing decomposition of many of the diatomic molecules into single atoms:  $\text{H}_2 \rightleftharpoons 2\text{H}$ . He has measured the percentage of molecules dissociated (at 760 mm.), and found that it varies from 0.33 per cent at  $2000^\circ$  to 13 per cent at  $3000^\circ$  and 34 per cent at  $3500^\circ$ . When the temperature falls, the atoms re-combine to form diatomic molecules.

It may also assist in making the matter clear if we note that the atomic weight of an element is the unit quantity of that particular variety of matter, *when it is in combination*. The unit quantity of the same variety of matter, when in the free state, as a *substance*, need not be the same. We should not expect it to be smaller, but it might easily be twice or more times as large.

**Replies to Questions about Difficulties.**—The beginner always becomes confused over one or more of the points raised by the following questions:

1. Why was 32 g. of oxygen taken as the standard for molecular weights, rather than 16 g.? Read p. 252 and footnote to p. 240.

2. If  $O_2$  is the smallest mass of oxygen, why do we have formulæ like  $H_2O$  and  $HClO$ ?  $O_2$  is the smallest mass of *free* oxygen, but in combination half as much occurs in many molecules. Read pp. 241, 250, and 251.

3. Why is not the atomic weight of an element ascertained by simply measuring the density of the elementary substance? Read pp. 251 and 261.

4. Can we not deduce the valence of an element from knowing the number of atoms in its molecule, and *vice versa*? Some molecular formulæ and valences are:  $H_2^I$ ,  $O_2^{II}$ ,  $Cl_2^I$ ,  $Zn^{II}$ , also Hg (univalent and bivalent),  $P_4$  (trivalent and quinquivalent) and  $S_8$  (bivalent and sexivalent). There is no relation, either observable or to be expected.

5. Do the molecular weights, oxygen = 32 and hydrogen = 2, mean that the molecules of oxygen are *larger* than are those of hydrogen? This is the ratio of their weights, but none of the phenomena discussed in this chapter are influenced appreciably by their relative sizes, and therefore none of them give any information on the subject. Read the footnote to p. 237.

**Exercises.**—1. The weight of 1 l. of gas at  $0^\circ$  and 760 mm. is 5.236 g. What is the density referred (a) to air (air = 1) and (b) to hydrogen, and (c) what is the molecular weight (pp. 233, 237)?

2. The density of a gas, referred to air, is 6.7. What is the weight of 1 l. (p. 233), and what is the molecular weight (p. 237)?

3. The molecular weight of a substance is 65. What is the density referred to air, and what is the weight of 1 l.?

4. If the molecular weight of oxygen were taken as 100, what would be the volume of the G.M.V. (p. 233)? What, on the same scale, would be the molecular weight of water, and what would be the atomic weights of hydrogen and chlorine (pp. 233, 241)?

## CHAPTER XIII

### APPLICATIONS OF MOLECULAR AND ATOMIC WEIGHTS. PROPERTIES OF ATOMS

*Applications: Interactions Between Gases.* — According to Avogadro's law, if we filled a succession of vessels of equal dimensions with different gases, and could arrest the motion of the particles and observe their disposition, we should find that the average distance from particle to particle would be the same in all cases. This would be true whether our vessels were filled with single gases, with homogeneous mixtures, or with gases in layers. Such being the case, if any chemical change is brought about in the mass which results in a multiplication of the molecules, it is evident that the volume will have to increase in order that the spacing may remain the same as before. If any chemical action results in a diminution of the number of molecules, then a shrinkage must take place in order that the spacing may be preserved as before. Thus, in a mixture of hydrogen and chlorine, according to our hypothesis, when interaction to produce hydrogen chloride occurs, neighboring molecules of hydrogen and chlorine simply exchange units, so that  $HH + ClCl$  becomes  $HCl + ClH$ . There being no alteration in the number of particles, no change in volume occurs. In the case of water, on the other hand,

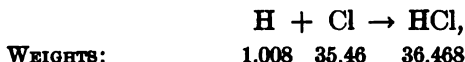


Since the oxygen molecules, which form a third of the whole, disappear into the molecules of hydrogen, the tendency to preserve spacing results in a diminution of the volume by one-third (p. 156). Thus Gay-Lussac's law would have followed as a natural inference from Avogadro's law, if the former, being more obvious, had not been discovered first.

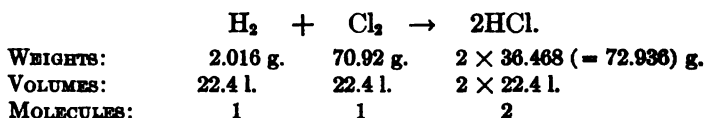
This method of looking upon chemical interactions between gases gives us the nearest sight which we can have of the behavior of the molecules themselves. We cannot perceive the individual molecules, but, in consequence of the spatial arrangement which they observe, the change in the whole volume of a large aggregate of

molecules enables us to draw conclusions at once in regard to the behavior of the single molecules in detail.

**Applications: Molecular Equations.**—To utilize the foregoing considerations, chemists **always employ in their equations the molecular formulæ** for the gases and easily vaporized substances concerned. Thus far, we have used the equation:

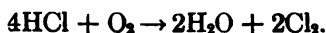


and the information it contained was exhausted when we had placed below the symbols the weights for which they stood. But the molecular equation is much more instructive. The following shows the interpretations to which the molecular equation is subject:

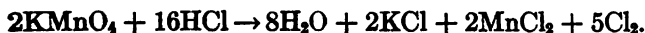


The weights, although doubled, show the same proportions, so that questions of weight are answered as easily as before. These weights, however, being molecular weights, or multiples thereof, can be translated at once into *volumes*, and questions about volumes can also be answered. Finally the relative numbers of each kind of molecules can be read from this equation, for the coefficients in front of the formulæ represent these numbers. Where no coefficient is written, 1 is to be understood. The application of these properties of molecular equations is illustrated below. Before applying these equations, however, we must first learn how to make them.

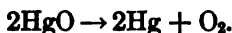
**Applications: The Making of Molecular Equations.**—To make a molecular equation, we first make an equation according to the rules already explained (p. 73). An equation like that given for the interaction of oxygen with hydrogen chloride (Deacon's process, p. 216):  $2\text{HCl} + \text{O} \rightarrow \text{H}_2\text{O} + 2\text{Cl}$ , is the result. Then we adjust the equation so that molecular formulæ are used throughout.  $2\text{Cl}$  becomes at once  $\text{Cl}_2$ . The oxygen, however, must also appear as  $\text{O}_2$ , or a multiple of this, in such equations. Hence the whole equation must be multiplied by 2:



Again, the equation for the preparation of chlorine from potassium permanganate and hydrochloric acid (p. 218) becomes:



Every equation containing an *odd* number of atoms of a substance whose molecules are *diatomic* must be multiplied by 2. Again, mercuric oxide decomposes to give mercury vapor and oxygen (p. 17), and the molecules of mercury are monatomic and those of oxygen diatomic, so we write:



Finally the formulæ of substances which are solid or liquid, and cannot be easily vaporized, are written in the simplest terms. Thus, since substances like the copper in the following equation are insoluble, the molecular weights of such substances are unknown, and their molecular formulæ likewise:  $2\text{Cu} + \text{O}_2 \rightarrow 2\text{CuO}$ . Furthermore, in the case of substances which can be volatilized, although the molecular weights and molecular formulæ may therefore be known, we do not usually employ the molecular formulæ if the substance is not used in the form of vapor in the laboratory. Thus, the molecular formula of phosphoric anhydride is  $\text{P}_4\text{O}_{10}$  (p. 88). But we generally make, and use, only the solid form, and not the vapor, in actual work. Hence the action with water is usually written as we have given it (p. 149), rather than in the form:  $\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4$ .

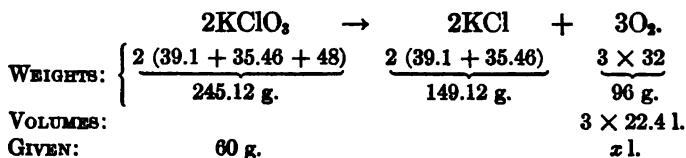
The applications of the properties of molecular equations (which will be used exclusively hereafter) may now be illustrated in detail.

**Applications: To Arithmetical Problems.**—1. When a problem in regard to **weights** of material used or produced in a given action is to be solved, the molecular equation is to be written and the weights inserted beneath the formulæ. The mode of calculation has been described already (p. 75).

2. When a problem involving **weights and volumes** is to be solved, the molecular equation is to be written, and both the weights and volumes are to be inserted. Note, however, that the volumes of the substances which are *in the gaseous condition* only are inserted.

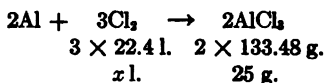
For example: What volume of oxygen is obtained from 60 g. of potassium chlorate? The molecular equation, made as shown above (p. 256), together with the full interpretation, are as follows:





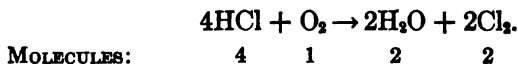
Observe that no volumes are given under the chlorate and chloride of potassium. This is because their volumes in the *gaseous* condition can be of no practical use, since they are solids which are melted, *but not vaporized* during this, or any action in which we employ them. Note also that the data *given* in the problem are inserted, and  $x$  l. is placed under the oxygen. Now, as to the problem in hand, it is concerned with a weight of potassium chlorate and a volume of oxygen. Reading from the equation, our information on *these* points is that 245.12 g. of potassium chlorate give 67.2 liters (observe that the *coefficients* are used, as well as the molecular weights, in these numbers) of oxygen at  $0^\circ$  and 760 mm., and the question is, What volume will 60 g. give? By proportion,  $245.12 \text{ g.} : 67.2 \text{ l.} :: 60 \text{ g.} : x \text{ l.}$ , where  $x = 16.4$  liters. If a different temperature and pressure had been specified, either the volume in the equation, or the answer, would have had to be converted by rule to the given conditions.

It saves time not to write out, as above, the whole interpretation, but only the parts required. For example, if the question is: What volume of chlorine is needed to give 25 g. of aluminium chloride, we may, if we choose, omit all the data excepting the volume of the chlorine and the weight of the aluminium chloride, thus:



The volume of chlorine required is  $3 \times 22.4 \times 25 \div (2 \times 133.48)$  liters. These illustrations show the method of calculating actual volumes (see Exercises 4, 5).

3. If the question concerns **relative volumes** only, then it is simplest to use the interpretation of the equation in terms of molecules. For example, What relative volumes of hydrogen chloride and oxygen are required in Deacon's process? The molecular equation is (p. 256):

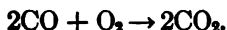


Since equal numbers of molecules of gases occupy equal volumes, the proportion 4 molecules of hydrogen chloride to 1 molecule of oxygen shows the ratio to be 4 : 1 by volume. Similarly, every 4 molecules of hydrogen chloride give 2 molecules of chlorine, so that the ratio of these substances by volume is 4 : 2, or 2 : 1.

In regard to the water, since that is not a gas at common temperatures, the question, if asked, must be more specific: What are the relative volumes of *steam* and chlorine in the product, as commonly delivered by the action at 400°? It is 2 : 2, or 1 : 1. What are the relative volumes of water and chlorine, after the products have cooled to room temperature? The water is no longer a gas, so that it occupies, relatively, almost no volume.\*

What is the total volume-change in the foregoing action above 100°? It is a change from 5 molecules to 4. The volume changes in the same ratio. But at 0° the volume-change is from 5 volumes to 2, for the water does not appreciably add to the volume of the products (see Exercises 6, 7).

4. When we know the molecular formulæ of the single substances concerned in an action, the equation can be made, and the relative volumes determined, without actual measurement. For example: What volume-change will be observed when a mixture of carbon monoxide and oxygen has exploded, and the temperature has once more reached that of the room? The molecular formulæ are CO, O<sub>2</sub>, and CO<sub>2</sub>. The equation representing the *weights* is  $\text{CO} + \text{O} \rightarrow \text{CO}_2$ . The molecule of oxygen, however, being O<sub>2</sub>, we cannot employ less than this quantity in a molecular equation, so that the equation becomes:



Three molecules, therefore, give two, throughout the whole mass, and therefore three volumes will become two, if the pressure and temperature are the same at the beginning and end of the action.

If we remember that all volatile compounds of carbon and hydrogen burn to form water and carbon dioxide, the molecular equation

\* Of course if an exact answer *must* be given, it can be given. But for this we require the weight and specific gravity of the product. Thus, 2H<sub>2</sub>O represents 2 × 18 g. of water. The sp. gr. of water is 1. Therefore the volume of water formed is 36 c.c. The volume of 2Cl<sub>2</sub> is 2 × 22.4, or 44.8 liters at 0°. The ratio of water to chlorine by volume at 0° is therefore 36 : 44.800. But, as a rule, we simply give the volumes of solids and liquids as *zero*, compared with those of the gases concerned in the same action.

for any such combustion may easily be made, and the volumes of all the materials ascertained. When water is a product, only its volume as steam is given by the equation (see Exercises 7, 8).

5. Knowing by heart the molecular formulæ of gaseous substances, as we must know them for many purposes, it is unnecessary to burden our minds with other data in regard to the **relative densities of gases**. Is hydrogen chloride  $\text{HCl}$  heavier or lighter than carbon dioxide  $\text{CO}_2$ ? These formulæ represent the weights of equal volumes (22.4 l.), namely 36.46 g. and 44 g., respectively. Hence the former gas is a little lighter. Remembering that the G.M.V. of air weighs 28.955 g. (Table, p. 233), we can compare the weight of any gas with that of air in the same way.

What are the relative weights of acetylene ( $\text{C}_2\text{H}_2$ , p. 241) and sulphur dioxide  $\text{SO}_2$  as compared with air? The G.M.V. cube holds formula-weights of the first two, namely 26 g. and 64 g., and 28.955 g. of air. Hence acetylene is a little lighter than air, and sulphur dioxide more than twice as heavy (see Exercise 9).

**Applications: To Cases of Dissociation.**—Several gases or vapors yield smaller values for their densities, and therefore molecular weights, when the densities are measured at higher temperatures. This indicates that the molecules have become lighter, and can only mean that decomposition has taken place in consequence of the heating. Behavior of this kind is shown both by compounds and by simple substances.

For example, **phosphorus pentachloride**  $\text{PCl}_5$ , although a solid, can be converted into vapor without much difficulty. Its molecular weight, if it underwent no chemical change during the volatilization, would be  $31 + 177.3 = 208.3$ . The density actually observed at  $300^\circ$  and 760 mm. pressure gives by calculation not much more than half this value. The direct inference from this is, that the molecules have only half the (average) weight that we expected: or, in other words, are twice as numerous as we expected. The explanation is found when we examine the nature of the vapor more closely. We find that it is a mixture of phosphorus trichloride and free chlorine, resulting from a chemical change according to the equation:  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ . The low value of the density thus tells us that dissociation has taken place. From the value of the density at various temperatures, we may even calculate the proportion of the whole material which is dissociated. At  $300^\circ$  it is 97 per cent; at  $250^\circ$ , 80 per cent; and at  $200^\circ$ , 48.5 per cent. Thus, when the temperature

is lowered, progressive recombination takes place and the proportion dissociated becomes less. Finally the vapor condenses and yields the original solid.

Again, sulphur boils at  $445^{\circ}$ , but is easily vaporized at a temperature as low as  $193^{\circ}$ , under very low pressure. At this temperature the density of the vapor gives the molecular weight 256 ( $= 8 \times 32$ ), and the molecular formula  $S_8$ . That is to say, the G.M.V. holds 256 g. of the vapor at  $193^{\circ}$ . At  $800^{\circ}$ , however, the density is only one-fourth as great, and the G.M.V. holds only 64 g. ( $S_2$ ). This means that 256 g. now occupy four times as large a volume as before, and the increase is additional to the effect of the mere thermal expansion, which is allowed for in the calculation and eliminated. Hence the molecules have dissociated. At  $1700^{\circ}$  the molecular formula is still  $S_2$ , so that this shows the limit of observed dissociation:  $S_8 \rightleftharpoons 4S_2$ . When the vapor is cooled, the density increases once more and at  $193^{\circ}$  recovers completely the greater value. Similar observations show that phosphorus vapor at  $313^{\circ}$  is all  $P_4$ , but at  $1700^{\circ}$  one-half of the molecules are  $P_2$ . Iodine vapor, up to  $700^{\circ}$ , is all  $I_2$ . Beyond this temperature the density diminishes, and when  $1700^{\circ}$  is reached the vapor is all  $I$ . Thus the molecules are diatomic at low temperatures and monatomic at high ones. The densities of oxygen, hydrogen, and chlorine are not measurably affected by heating to  $1700^{\circ}$ , so that their diatomic molecules exist from temperatures far below  $0^{\circ}$  up to  $1700^{\circ}$ , and are evidently very stable. For observations on hydrogen above  $1700^{\circ}$ , however, see p. 253.

**Applications: Finding the Atomic Weight of a New Element.** — By way of reviewing the principles explained in this chapter, let us apply them to the imaginary case of a newly discovered element. The bromide of the element is found to be easy of preparation and to be volatile. The bromide contains 30 per cent of the element, and therefore 70 per cent of bromine, and its vapor density referred to air is 11.8. The analysis can always be made much more accurately than the measurement of vapor density, so that the two former numbers are more trustworthy than the last.

To find the equivalent of the element, that is, the amount combined with 79.92 parts (the equivalent, and also the atomic weight), of bromine, we have the proportion  $70 : 30 :: 79.92 : x$ , from which  $x = 34.3$ . The atomic weight must be this, or some small multiple of it.

The G.M.V. of air weighs 28.955 g. (p. 233). Hence the same

volume of the vapor of this bromide, which is 11.8 times as heavy as air, will weigh  $28.955 \times 11.8$ , or 341.67 g. This is therefore the molar weight of the compound.

Now 30 per cent of this is the new element:  $341.67 \times 30 \div 100 = 102.5$ . Three times the equivalent weight is the multiple nearest to this number,  $3 \times 34.3 = 102.9$ , the difference being due to error in determining the density. So long as no other volatile compound is known, we adopt this as the atomic weight. The rest of the molar weight ( $239.76 = 3 \times 79.92$  parts) is bromine. Thus the formula of the compound is  $\text{ElBr}_3$ , and from this we see that the element is trivalent.

In case no volatile compound of the element can be formed, the weight combining with 79.92 parts of bromine is measured as before. Then some of the free simple substance is made, say by electrolysis, and its specific heat is determined. The sp. ht. is about 0.063. Application of Dulong and Petit's law then gives the atomic weight. The product  $34.3 \times 0.063$  is equal to 2.161. Hence, the equivalent must be multiplied by 3 to give the atomic weight, for this raises the product to 6.48, which is within the limits. Thus the value of the atomic weight is 102.9, as before.

#### PROPERTIES OF ATOMS

There is danger that one may attribute to atoms properties which they do not possess. It is sometimes said that an atom of an element is the smallest particle of that element which possesses the same properties as a larger portion of the same element. This is an ill-considered statement. For example, an atom of mercury, in mercury vapor, has the perfect elasticity of a molecule, but a mass of frozen mercury has a limited degree of elasticity, like any other piece of matter. We should note, therefore, the properties which the experimental work thus far described has shown atoms to possess.

**Properties of Atoms.** — Atoms move from one state of combination to another **without alteration in their mass**. Since they may be restored to their free condition and recombined as often as we choose, without impairment of their individuality, **each kind must be composed of a distinct variety of matter**.

The conception of valence (p. 130) suggests that some atoms unite with but *one* other atom, habitually ( $\text{NaCl}$ ). Some, however, unite with two of the first kind ( $\text{ZnCl}_2$ ), or with one other of their

own kind ( $\text{ZnO}$ ), still others with three atoms of the first kind ( $\text{AlCl}_3$ ), and so forth. In other words, it involves the assumption that **each kind of atom has a limited capacity for holding other atoms in combination**. Thus, taking the most crudely mechanical view of the matter, we might suggest that there is a limit to the number of points at which atoms may be attached to one another. When one atom of chlorine is attached to one of sodium, the combining capacity of each is exhausted. When one atom of hydrogen is attached to one atom of oxygen, one combining capacity of the oxygen still remains ( $\text{H} - \text{O} -$ ), and can be satisfied by one more atom of hydrogen or of some other element.

Atoms of the same kind can combine with one another. Thus we have  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{N}_2$ , and so forth. But many kinds of atoms lack this quality. The molecules of metals, so far as we have been able to ascertain their nature, are monatomic, *e.g.*, K, Na, Hg, Zn, Cd. Then some atoms, those of the noble gases (*q.v.*), refuse to combine with any other atoms whatever, *e.g.*, He, Ne, Ar, Kr, Xe, Rn.

Again, certain compounds, similar in composition, such as barium peroxide  $\text{BaO}_2$  and manganese dioxide  $\text{MnO}_2$ , show different chemical behavior. The former of these when treated with sulphuric acid gives hydrogen peroxide (*q.v.*), while the latter gives only water and oxygen. If it were merely a question of composition, the substances should behave alike. So, also, we often have two or more compounds identical in molecular weight, and in the elements and numbers of units which they contain, which are nevertheless totally different in physical and chemical properties. To account for this difference we have found it convenient to suppose that, although the atoms contained in the two or more kinds of molecules are of the same numbers and kinds, **the atoms are in different geometrical arrangement towards one another**. Sometimes one of these substances can be made directly from the other, and this gives us that variety of chemical change which was named internal rearrangement (p. 20). Thus, ammonium cyanate  $\text{NH}_4\text{CNO}$ , when heated in aqueous solution, turns into urea  $\text{CO}(\text{NH}_2)_2$ , a substance with totally different chemical properties.

Finally, the atoms of uranium, thorium, radium, and some other elements, **disintegrate spontaneously**, giving off atoms of helium and electrons (see Radioactivity), so that some kinds of atoms are unstable.

To sum up: Each kind of atom has a specific mass, and consists as a whole of a specific kind of material. Each atom, of the kinds

that can enter into combination, has a maximum capacity for holding other atoms (valence). When there are more than two atoms in the molecule of a compound, there is often more than one way of connecting them so as to satisfy the valence, and thus two or more different substances of the same composition may exist. Some atoms are unstable, and we know something of the structure of all atoms (see Chap. XXII).

**Properties of Compounds not Explained by Properties of Atoms.**—In one direction, namely, that of accounting for the properties of compounds, no attempt has been made to adapt the atomic viewpoint so as to explain the facts. Thus, two hydrogen atoms in a molecule give a gas almost insoluble in water; two chlorine atoms, a gas which is moderately soluble; but one of each gives hydrogen chloride, which dissolves in water in extraordinary quantities. So also, colorless substances give, by chemical union, strongly colored ones, and odorless substances, by chemical union, strongly odorous ones. Putting pieces of iron and sulphur side by side causes absolutely no change in the properties of either. And yet the atomic viewpoint compels us to assume that if the particles are made fine enough, and placed close enough to one another, the individual properties of the constituents will entirely disappear. Hitherto we have failed to think of any qualities which might be attributed to the atoms in order to account for facts of this class. Why should oxygen  $O_2$  and ozone  $O_3$  be so different in behavior although the atomic viewpoint hints at nothing but a substitution of three atoms for two? What atomic properties shall account for the difference between red and yellow phosphorus?

**Definitions Should be in Experimental Terms.**—Definitions are often stated in terms of atoms and molecules. For example: A **physical change** is one in which the relations amongst the molecules are altered, but the molecules themselves are not affected in any way; while a **chemical change** is one in which the molecules themselves are decomposed, or their contents are rearranged. State this definition to some one, and instruct him then to examine a vessel of boiling water, with the definition in mind, and report whether the process of vaporization is physical or chemical. He will report that he could not perceive either molecules or atoms in the vessel, and therefore cannot answer the question. Definitions like the above can be memorized and, with the help of the imagination, they

can be understood, but they are not directly applicable to any question arising in the laboratory.

**Again, the law of definite proportions:** Each species of molecules contains the same kind and number of atoms. We cannot directly count and classify the atoms in ten specimens of potassium chlorate, to ascertain whether, in this respect, they are all alike. Such definitions require elaborate translation into other terms before they can be connected with any practicable method of verifying, illustrating, or employing them. Chemistry is a practical subject, and the statement and definitions should all be in terms of experimental facts and phenomena, and should never require translation into other terms before they can be put to practical use. Hence the definitions we have given (*cf.* p. 54) have all been in terms of experiments.

**Exercises.** — 1. The chloride of a new element contains 38.11 per cent of chlorine and 61.89 per cent of the element. The vapor density of the compound referred to air is 12.85. What is the atomic weight of the element, so far as investigation of this one substance can give it (p. 261)? What is its valence?

2. In future nothing but molecular formulæ of free elements must be used (p. 250). Write in molecular form ten of the equations involving gases which are found in the preceding chapters.

3. If a new form of oxygen were found, such that one volume of it required four volumes of hydrogen to produce water, what would be its molecular formula (p. 252)? What would be the weight of 22.4 l.?

4. What volume of oxygen at 10° and 750 mm. is obtainable by heating 50 g. of barium peroxide (pp. 82, 257)?

5. What volume of oxygen at 20° and 760 mm. is required to convert 16 g. of iron into dehydrated rust  $\text{Fe}_2\text{O}_3$  (p. 257)?

6. Write out the molecular equations for the interactions of methane and chlorine giving  $\text{CH}_3\text{Cl}$ ; and for the burning of phosphorus (vapor) in oxygen (p. 257). Deduce the volume relations of the initial substances, and of the products, at 0° and 100° in each case.

7. Write out the molecular equations for the interactions of acetylene and oxygen (p. 259), and of alcohol vapor (b.-p. 78°) and oxygen. Deduce the volume relations of the initial substances and of the products at 0° and at 100° in each case.

8. The molecular weight of cyanogen is 52.08. What is its den-



sity referred to air, and what the weight of 1 l. at  $0^{\circ}$  and 760 mm.? It contains 46.08 per cent carbon and 53.92 per cent nitrogen. What is the formula of the substance (p. 72)? Exploded with oxygen it forms carbon dioxide and free nitrogen. What will be the relative volumes of the materials before and after the interaction (p. 259)?

9. What are the relative weights of equal volumes of hydrogen sulphide  $H_2S$ , and hydrogen iodide  $HI$ , compared with air (p. 258)?

10. At  $1700^{\circ}$  the average molecular weight of phosphorus is 91 (p. 261). What percentage of molecules of  $P_4$  has been dissociated into  $P_2$ ?

11. Show that, if an element has more than one equivalent weight, the atomic weight must be some multiple of each of the equivalents by a whole number.

12. Prove that 16 is preferable to 8 for the atomic weight of oxygen, because the smaller number involves a fractional value for the atomic weight of hydrogen.

13. In previous chapters our definitions have been experimental. In imitation of the definitions of the law of definite proportions and of valence (p. 264), give theoretical definitions of the following, in terms of the atomic hypothesis: (a) Multiple proportions, (b) chemical unit weight, (c) molecular weight, (d) element, (e) compound, (f) symbol, (g) formula, (h) equation.

14. Criticize the definitions: (a) The atomic weight of an element is the smallest portion of that element which takes part in chemical change. (b) An atom is the smallest particle that can be conceived.

15. Define all the varieties of chemical change (p. 21) in terms of the atomic hypothesis.

## CHAPTER XIV

### THE HALOGEN FAMILY

#### FLUORINE, CHLORINE, BROMINE, IODINE

THE elements to which we have so far devoted most attention have been oxygen, hydrogen, and chlorine. If we recall the chemical properties and relations of these elements we shall recognize the fact that they all possess very distinct individualities.

*The Chemical Relations of Elements.* — Hydrogen is the substance (p. 127) which unites readily with oxygen and chlorine, less readily with other non-metals, and scarcely at all with metals. Oxygen and chlorine resemble one another somewhat in the greatness of their chemical activity and the variety of free elements with which they are capable of uniting, but differ markedly in what we have called their chemical relations (p. 226). The resulting compounds belong, in fact, to quite different classes — oxygen forms oxides, chlorine forms chlorides — and elements are considered similar only when they resemble one another in chemical relations, and produce, by combination with the same element, compounds having similar chemical properties. Thus the common oxide of hydrogen, water, is a neutral substance, and is chemically rather indifferent. The chloride of hydrogen in aqueous solution is a strong acid and is chemically very active.\* If all the other chemical elements differed from one another as much as do these three, the study of the chemical elements would be tedious and tiresome, since we should be denied the satisfaction of tracing resemblances, and the elements would be incapable of classification. In reality, however, we find that they are not incapable of being grouped together in sets. They are classified according to the kind of substances with which they combine and the chemical nature of the products. In some families the resemblance is close, in others

\* The difference between oxides and chlorides is seen in their behavior. Thus, oxides often unite with water to form acids or bases (p. 149). Chlorides do not unite with water to form new substances with marked characteristics (cf. p. 152). The chlorides of metallic elements are designated salts (p. 214).

less close. The present group is of the former class, and will serve, therefore, as a convenient beginning in the work of tracing relations between the elements and in classifying the facts of descriptive chemistry.

**The Chemical Relations of the Halogens.** — The bromide (NaBr), iodide (NaI), and, to a less extent, the fluoride (NaF), of sodium, resemble sodium chloride (NaCl) in composition, appearance and chemical behavior. From this fact, chlorine, bromine, iodine, and fluorine are known as the **halogens** (Gk. ἅλς, salt; γεννᾶν, to produce), and their compounds are named the **halides**. The halogens, as the above formulæ show, are univalent. They all form compounds with hydrogen, and these compounds closely resemble hydrogen chloride. For example, they are colorless, they are gases (with the exception of hydrogen fluoride which is a very volatile liquid), they are very soluble in water, and their solutions are acids. Other relations will be given in a summary at the end of the chapter.

### BROMINE

**Occurrence.** — The compounds of chlorine, bromine, and iodine usually occur together in nature, while the compounds of fluorine are not found in the same sources. Bromine occurs chiefly in the form of the bromides of sodium and magnesium, in the upper layers of the natural beds of rock salt. Liebig made it from this source and a little later Ballard (1826) made it also and recognized it as a new element.

**Preparation.** — In the chemical point of view there are three distinct ways in which bromine is made. 1. The first of these is closely related to a common method of preparing chlorine (p. 220). As

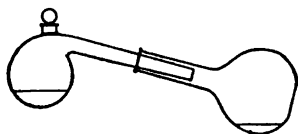


FIG. 94.

hydrobromic acid, unlike hydrochloric acid, is not formed extensively in connection with any chemical industry, potassium bromide is treated in a retort (Fig. 94) with concentrated sulphuric acid, and the product is oxidized with powdered manganese dioxide in one operation. For the equation, see next section. Bromine being a volatile liquid, while the sulphates of potassium and manganese are involatile, its vapor passes off when the above mixture is heated. It is condensed in a flask or a worm-tube surrounded by cold water.

2. The second method of preparing bromine depends on the fact

that chlorine is a more active element and *displaces* bromine from combination. When, therefore, chlorine is passed into a solution of potassium or sodium bromide, potassium or sodium chloride is formed and the bromine liberated:



When the liquid is warmed, the bromine passes off along with a part of the water, and may be condensed as before.

3. Aqueous solutions of soluble bromides may be decomposed by means of a current of electricity. The bromine is set free at the positive electrode.

The bromine of commerce is manufactured in the first two of these ways. Two-thirds of the world's supply is obtained from Stassfurt, where, after the extraction of the potassium chloride from the impure carnallite  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , the mother-liquor is found to contain the more soluble sodium and magnesium bromides in considerable quantities. The warm mother-liquor trickles down over round stones in a tower. The chlorine is introduced from below and dissolves in the liquid. The bromine is thus liberated and passes off as vapor. A part of our supply of bromine is obtained from the brines of Ohio, West Virginia, and Kentucky. Here the liquid, after most of the common salt has been removed by crystallization, is assayed to ascertain the quantity of bromine which it contains. It is then treated with the calculated amount of sulphuric acid necessary for the action, and manganese dioxide is added gradually. In Michigan the brines are treated with electrolytic chlorine. The quantity produced in America in 1914 was 288 short tons.

### ***Partial Equations, a Plan for Making Complex Equations.***

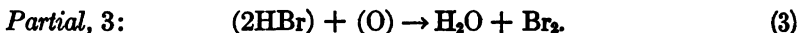
— When an equation involves *more than two* initial substances or products, as does the one given above for the first method of preparing bromine, it cannot readily be worked out by the method formerly recommended (p. 73). After the formulæ of all the substances, on both sides, have been set down, it is difficult to hit upon the proper numerical factors required to balance the equation. In such cases a good plan is to select *two* of the initial substances and make a **partial equation** showing part of the action and including at least one actual product. Any unused units (not constituting a product) are then set down also and treated as a balance. Thus the first two of the substances named will furnish potassium-hydrogen sulphate:



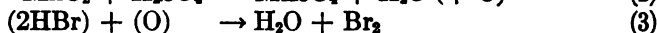
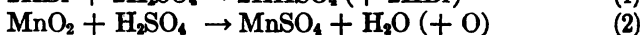
Similarly, the manganese dioxide and sulphuric acid will give manganous sulphate:



We then perceive that the bromine must come from the oxidation of the first balance by the second:



The third partial equation shows that  $2\text{HBr}$  will be needed for the amount of O obtainable from  $\text{MnO}_2$ , so we go back to (1) and multiply it by two throughout:



When we now add the real substances used and produced, as they occur in these partial equations, and leave out the balances, which have been adjusted so as to cancel one another, we obtain the final equation for the action. It must be observed that this subdivision of the action into parts is a purely arithmetical device, used solely to simplify the arithmetical process of writing the equations, and is not intended to imply that the chemical change itself follows these or, indeed, any stages. It happens that the three partial equations we have used in this illustration all represent interactions which can take place separately. But the arithmetical value of the device does not depend upon this. The partial equations made for purposes like the present one are often purely fictitious. It is still true, however, that we are aided in the selection of partial actions at each step by following some plausible theory as to stages for the action which, if there were any, would be chemically conceivable.

**Physical Properties.**—Bromine is a dark-red liquid (sp. gr. 3.18). It boils at  $59^\circ$ , forming a deep-red vapor, and even at ordinary temperatures gives a high vapor pressure (150 mm. at  $18^\circ$ ) and evaporates quickly. When cooled it forms red, needle-shaped crystals (m.p.  $-7.3^\circ$ ). A saturated aqueous solution (**bromine-water**) at ordinary temperatures contains 3 parts of bromine in 100 parts of water. The element is much more soluble in carbon bisulphide, alcohol, and other organic solvents. Up to  $750^\circ$ , the G.M.V. weighs 160 g., corresponding to  $\text{Br}_2$ , against 28.955 for air.

Bromine (Gk. *βρῶμος*, a stench) has a most pungent odor. It has a very irritating effect on the mucous membrane of the nostrils and throat. If spilled upon the hands it has a most destructive action upon the tissues and leaves sores which are liable to infection.

Free bromine has no effect upon starch emulsion (see Iodine).

**Chemical Properties.** — The molecules of bromine are less stable than are those of hydrogen, oxygen, or chlorine. At 1050° the G.M.V. weighs 150.5, and dissociation into Br has begun.

Bromine unites directly with hydrogen to form hydrogen bromide HBr, but the mixture of the gases is not explosive, and the union is much slower than in the case of chlorine.

Bromine forms compounds directly, both with non-metals, like phosphorus and arsenic, and with most of the metals, which catch fire when thrown into the vapor. Towards unsaturated substances and organic compounds it behaves like chlorine (*q.v.*). In all cases the interaction is less violent than when chlorine is used, and the element is displaced from combination with hydrogen and with the metals by free chlorine.

Silver bromide is the sensitive material in photographic plates, and potassium and sodium bromides are used as sedatives in medicine. Bromine is required in large quantities in the manufacture of intermediate products used in the preparation of organic dyes.

### HYDROGEN BROMIDE HBr

**Preparation.** — It might be expected that the most convenient way of producing this compound would be similar to that used in preparing hydrogen chloride, namely, by the action of concentrated sulphuric acid upon some common bromide such as potassium bromide ( $\text{KBr} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{HBr} + \text{KHSO}_4$ ). We find, indeed, that at first a colorless gas is given off, which fumes strongly in the air just like hydrogen chloride, and is the required substance. Almost immediately, however, the gas acquires a yellow and then a brown tinge, and we discover that free bromine is being produced at the same time. If we examine the gas still further, we recognize also the presence of sulphur dioxide. It is impossible, therefore, to produce hydrogen bromide free from those two impurities by this action.

The origin of the bromine and sulphur dioxide which complicate this chemical change may readily be traced. Hydrogen bromide is less stable than hydrogen chloride, and its hydrogen can more easily

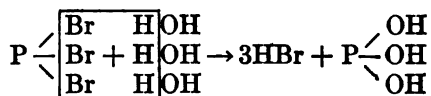
be removed by the action of substances containing oxygen. In this case the sulphuric acid acts as the oxidizing agent, yielding oxygen, sulphur dioxide, and water ( $\text{H}_2\text{SO}_4 \rightarrow \text{O} + \text{SO}_2 + \text{H}_2\text{O}$ ). Thus the two extra gaseous products are seen to be formed by a change proceeding parallel with the main action:



The simultaneous occurrence, in this fashion, of two more or less independent actions in the same vessel is not uncommon. Since the HBr is first liberated, and then oxidized, these two actions are called consecutive actions. The speeds of such actions may be differently affected by temperature. Thus, here, the second action seems to become more extensive as the temperature rises (see Chap. XXIII).

Since all acids decompose all salts more or less, by use of an acid which does not give up its oxygen so readily, such as phosphoric acid, pure hydrogen bromide may be obtained ( $\text{KBr} + \text{H}_3\text{PO}_4 \rightarrow \text{HBr} + \text{KH}_2\text{PO}_4$ ). The small solubility of the salt in concentrated phosphoric acid retards the interaction (p. 207) and makes the evolution of the gas very slow, however.

Pure hydrogen bromide is best prepared by hydrolysis (p. 210) of phosphorus tribromide. When bromine and phosphorus are mixed, a violent union of the two elements takes place, producing phosphorus tribromide  $\text{PBr}_3$ . This substance, which is a colorless liquid, is in turn broken up with great ease by water, producing phosphorous acid, which is not volatile, and gaseous hydrogen bromide:



In practice, those two actions are carried on simultaneously. To diminish the vigor of the interaction, red phosphorus is taken instead of yellow, and is mixed with two or three times its weight of sand in a flask (Fig. 95). A small quantity of water is added. Excess of water must be avoided, as the hydrogen bromide produced is extremely soluble, and would therefore be retained in the flask instead of being disengaged as gas. The bromine is placed in the dropping funnel, and admitted, a little at a time, to the mixture. The gas produced is

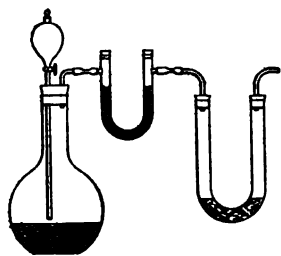
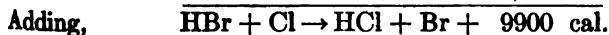
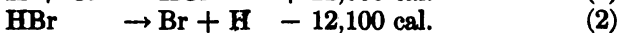
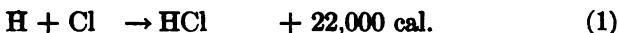


FIG. 95.

passed through a U-tube containing glass beads mixed with red phosphorus. The latter combines with any bromine which may have escaped chemical change and has been carried along with the gas. The second U-tube, containing water, may be attached when a solution of the gas is required. The gas may be collected in a jar by upward displacement of air.

**Physical Properties.**— Hydrogen bromide is a colorless gas with a sharp odor. It is two and a half times as heavy as air (molar weight, 81 g.). It is easily reduced to the liquid condition (b.p.  $-69^{\circ}$ ). It is exceedingly soluble in water, and in contact with moist air condenses the water vapor to a fog of liquid particles. When distilled, the solution in water behaves like that of hydrogen chloride (p. 211). It loses mainly either water or hydrogen bromide, according as it is dilute or exceedingly concentrated, until an acid of constant boiling-point ( $126^{\circ}$  at 760 mm. pressure), containing 48 per cent of hydrogen bromide, passes over. Pure hydrogen bromide, whether in the gaseous condition or in the liquefied form, is a nonconductor of electricity.

**Chemical Properties.**— The chemical properties of hydrogen bromide are similar to those of hydrogen chloride (p. 212). It is somewhat less stable, and dissociation into its constituents begins to be noticeable at  $800^{\circ}$ . When free from water, it is not an acid (see below). The gas interacts vigorously with chlorine, hydrogen chloride and free bromine being produced, and much heat is evolved by the change,  $2\text{HBr} + \text{Cl}_2 \rightarrow 2\text{HCl} + \text{Br}_2$ . The heat produced by the union of hydrogen and bromine vapor is 12,100 calories. This is much less than the amount produced by the union of chemically equivalent quantities of hydrogen and chlorine (22,000 calories). When chlorine displaces bromine from hydrogen bromide, the heat evolved is found to be the difference between these two numbers. Using the rule of constant heat summation (p. 100), we write equation (2) so that HBr is on the same side with Cl (with which it interacts), and the products of the equation required (HCl and Br) are both on the right:



The 12,100 calories are produced by the union of gaseous bromine with hydrogen, and the final result is, therefore, that for the produc-



tion of *gaseous* bromine. If the heat of formation of liquid bromine is required, the latent heat of vaporization of bromine (7296 calories), which will be evolved when the element condenses, must be added.

**Chemical Properties of Hydrobromic Acid  $\text{HBr}$ , Aq.** — The solution of the hydrogen bromide in water is an active acid (*cf.* p. 212). It conducts electricity extremely well. In contact with metals above hydrogen in the order of activity (p. 129), and with oxides of metals, and hydroxides of metals, it behaves exactly like hydrochloric acid (p. 213). In the first case, hydrogen is set free and the bromide of the metal produced. In the other two cases, water and the bromides of the metals are produced. For example:  $\text{Zn(OH)}_2 + 2\text{HBr} \rightarrow \text{ZnBr}_2 + 2\text{H}_2\text{O}$ . Oxidizing agents set bromine free from hydrobromic acid, even sulphuric acid, which does not act upon hydrochloric acid, being able to produce this result. Chlorine dissolved in water displaces bromine from hydrobromic acid and from soluble bromides with ease (*test* for bromides).

### IODINE $\text{I}_2$

**Occurrence.** — Iodine, like bromine, occurs in sea-water, although in much smaller quantities. About one-fifth of it is in living algæ and four-fifths in soluble organic compounds, presumably decomposition products from dead algæ, and little as mineral iodides. Certain species of sea-weed, known in Scotland as kelp and in Normandy as *varec*, remove it from water, and use it as a constituent in complex organic compounds which they contain. The ash of the sea-weed sometimes contains as much as two per cent, or even more. The chief source of iodine, however, is Chile saltpeter  $\text{NaNO}_3$ , in which it is present in the form of 0.2 per cent of sodium iodate  $\text{NaIO}_3$ . The largest proportion of iodine in the human body is in the thyroid gland. In diseases like goitre and cretinism, where the thyroid is ill-developed, injection of a substance called **iodothyline**, extracted from sheep's thyroids, produces marked improvement.

**Preparation.** — 1. In factories where the iodine is extracted from sea-weed, the latter is carbonized in retorts. The residue is extracted with water, and the solution is evaporated so as to permit the deposition of the sodium chloride and sodium sulphate which it contains. The sodium iodide, being very soluble, remains in the mother-liquor. This is then treated with manganese dioxide and

sulphuric acid. The quantity of manganese dioxide is carefully measured so as to be just sufficient to set free the iodine contained in the liquid, without proceeding farther to the liberation of the chlorine which it contains in much larger amounts. When the mixture is heated, the iodine passes off in the form of vapor, and is condensed in a suitable receiver. The action (*cf.* pp. 220, 270) is:



2. In France the treatment is similar, excepting that chlorine is used to liberate the iodine in the last stage ( $2\text{NaI} + \text{Cl}_2 \rightarrow 2\text{NaCl} + \text{I}_2$ ). The quantity is adjusted so that excess may not be employed. The iodine, being insoluble, forms a dense precipitate and, when the liquid is pressed out, it remains behind in the form of a paste.

3. Electricity could also be used for the decomposition of this mother-liquor. The iodine is set free at the positive electrode.

4. When the sodium nitrate has been crystallized out of the aqueous extract from the Chile saltpeter, the mother-liquor is treated with sodium sulphite and sodium bisulphite:



The iodine, being insoluble, is precipitated.

In all cases the iodine is purified by distillation with a little powdered potassium iodide. It condenses in the solid form directly, in glittering, black plates (sublimed iodine). The distillation of a solid body, when a condensation takes place directly to the solid form, is spoken of as **sublimation**.

**Physical Properties.** — Iodine (Gk. *ἰωδῆς*, like a violet) is a solid substance (sp. gr. 5), exhibiting large, black crystalline plates of rhombic form. It melts at  $114^\circ$ , and boils at  $184^\circ$ . The vapor has at first a reddish-violet tint and, on being more strongly heated, becomes deep blue (see next section).

Iodine is very slightly soluble in water (about 1:6000) and the solution has a scarcely perceptible brown tint. It is much more soluble in carbon disulphide (p. 189) and in chloroform, in which it gives violet solutions. In alcohol and ether it gives solutions which are brown. The brown color is attributed to the fact that the iodine is in a condition of feeble combination and not simply in solution. These liquids become violet when heated. An aqueous solution of potassium iodide, hydrogen iodide, or any other iodide, has likewise the power to take up large quantities of iodine. Here the formation

of definite compounds (such as,  $\text{KI} + \text{I}_2 \rightleftharpoons \text{KI}_3$ ), by a reversible action, accounts for the amount of iodine which appears to be in solution.

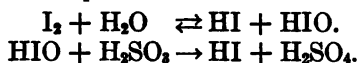
The behavior of free iodine towards starch forms a distinctive test for both substances (*cf.* p. 6). When the pale-brown aqueous solution, for example, is added to a filtered starch emulsion, a deep-blue color is produced. The same action is used as a test for starch. This blue material is not a chemical compound. The iodine is adsorbed by the starch, which is in colloidal suspension (*q.v.*).

**Chemical Properties.**—The molecular weight of iodine, ascertained by weighing the vapor at temperatures from the boiling-point up to  $700^\circ$ , is 253.8. The atomic weight being 126.92, the molecule contains two atoms. Beyond  $700^\circ$ , the vapor diminishes in density more rapidly than Charles' law would lead us to expect, and at  $1700^\circ$  the molecular weight has fallen to 127 (*cf.* p. 261). As the vapor is heated, a larger and larger proportion of the molecules is broken up, until the decomposition has become complete. As in all cases of dissociation, when the vapor is cooled the atoms recombine to form molecules. This is the most notable case in which we encounter both the monatomic and the diatomic forms of the same element. The heat given out when the atoms reunite to form the molecules is very considerable ( $2\text{I} \rightleftharpoons \text{I}_2 + 28,500 \text{ cal.}$ ), indicating that the chemical union of two atoms of identical nature may be as vigorous as that of two atoms of different chemical substances. The heat of union of atomic hydrogen (p. 253), however, is even greater ( $2\text{H} \rightleftharpoons \text{H}_2 + 90,000 \text{ cal. at const. press.}$ ). The monatomic and diatomic forms of iodine should be distinct chemical substances, and if the investigation of the behavior of the former were not hampered by the very high temperature at which alone it exists, it would doubtless be found to exhibit different chemical properties.

Iodine unites very slowly with hydrogen. Iodine unites directly with some non-metals and with the majority of the metals. When phosphorus is presented in the yellow form, the action takes place spontaneously without the assistance of heat. Both chlorine and bromine displace iodine from combination with hydrogen and the metals ( $2\text{HI} + \text{Br}_2 \rightarrow 2\text{HBr} + \text{I}_2$ ). The action may be brought about either with the substances in dry form or with their aqueous solutions.

Iodine in water, like chlorine in water, constitutes an oxidizing agent, although the former is much the feebleness of the two. The

hypo-iodous acid, formed in minute amounts at a time, converts sulphurous acid (*q.v.*) into sulphuric acid:



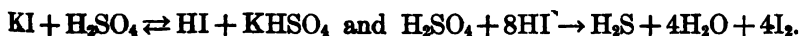
In analytical chemistry a solution of iodine in potassium iodide, containing a known proportion of dissolved iodine (a **standard solution**), is used for estimating the quantity of an oxidizable substance present in a given specimen. The amount of oxidizable substance present is measured by the quantity of the standard iodine solution which can be decolorized and suffer removal of its iodine. This method is known as **iodimetry**.

Iodine and its compounds are much *used* in the arts and in medicine. Iodine is applied in alcoholic solution (tincture of iodine) for the reduction of some swellings, and as an antiseptic. It is required in making iodoform  $\text{CHI}_3$ , and the iodides of potassium, rubidium, and sodium, which are used in medicine. Hydriodic acid  $\text{HI}$ , *Aq* is used to promote secretion in the lymphatic system. The emulsion used in making photographic dry-plates contains silver iodide  $\text{AgI}$ .

#### HYDROGEN IODIDE $\text{HI}$

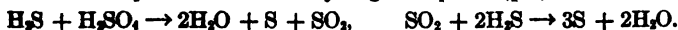
**Preparation.** — The direct union of hydrogen and iodine cannot be employed in preparing pure hydrogen iodide (see p. 306). The union is slow, and incomplete. At  $445^\circ$ , only 79 per cent of the elements unite, because the action is reversible.

The action of concentrated sulphuric acid upon potassium or sodium iodide is equally inapplicable. In this case, as in that of hydrogen bromide (p. 272), the hydrogen halide reduces the sulphuric acid, and much free iodine is formed. Here, on account of the greater ease with which hydrogen iodide parts with its hydrogen, the reduction of the sulphuric acid is much more complete, the product being hydrogen sulphide  $\text{H}_2\text{S}$ . The actions, which are consecutive (p. 272), are:



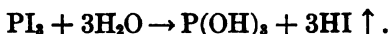
As soon as the heat produced by the action has raised the temperature sufficiently, hardly any of the hydrogen iodide escapes oxidation.\*

\* When much sulphuric acid is used, sulphur dioxide and free sulphur are formed also. This is in consequence of a secondary action of the hydrogen sulphide, as it passes up through the excess of sulphuric acid, and of the sulphur dioxide so formed upon the excess of hydrogen sulphide (*q.v.*):



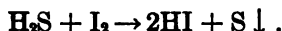
Powdered sodium iodide and concentrated phosphoric acid (*cf.* p. 272), when warmed, give pure hydrogen iodide very slowly:  $\text{NaI} + \text{H}_3\text{PO}_4 \rightleftharpoons \text{HI} \uparrow + \text{NaH}_2\text{PO}_4$ . This action was formerly used in preparing the gas.

The **best method** is one similar to that described under hydrogen bromide. Phosphorus and iodine unite directly to form  $\text{PI}_3$ . This is a yellow solid which is violently *hydrolyzed* by water and gives phosphorous acid and hydrogen iodide:



If excess of water, which dissolves hydrogen iodide, is avoided, the latter goes off in a continuous stream in a gaseous condition. The mixture of iodine (in excess of the amount required for  $\text{PI}_3$ ) and red phosphorus is placed in the flask (Fig. 95) and the water in the funnel.

Still **another method** of making hydrogen iodide is frequently employed when a solution of the gas in water is required, and not the gas itself. Powdered iodine is suspended in water, and hydrogen sulphide gas (*q.v.*) is introduced through a tube in a continuous stream. The iodine dissolves slowly in the water,  $\text{I}_2$  (solid)  $\rightleftharpoons$   $\text{I}_2$  (dissd), and acts upon the hydrogen sulphide, which likewise dissolves,  $\text{H}_2\text{S}$  (gas)  $\rightleftharpoons$   $\text{H}_2\text{S}$  (dissd). Sulphur separates in a fine powder,  $\text{S}$  (dissd)  $\rightleftharpoons$   $\text{S}$  (solid), and hydrogen iodide is formed in accordance with the equation:



This action takes place, however, only in presence of water, although the water does not appear in the equation. The solution is freed from the deposit of sulphur by filtration, and may be concentrated to 57 per cent of hydriodic acid by distilling off the water.

The theory of the last method is worthy of attention. It will be seen that while iodine has little tendency to unite with free hydrogen, it is here able to decompose a compound containing hydrogen, in order to secure this element. It is enabled to do this by the fact that the very large amount of heat given out by the mere solution of hydrogen iodide in water converts the action, which would otherwise be endothermal, into an exothermal one. In the absence of water, the reverse of the above action takes place with ease. In presence of water, however, the great heat of solution (p. 202) of the hydrogen iodide (+19,200 cal.) more than balances the heat absorbed by the chemical

change, and the action as a whole takes place with evolution of heat (see, also, Preparation of hydrogen sulphide):



**Physical Properties.** — Hydrogen iodide is a colorless gas with a sharp odor. Its molecular weight is 128, and it is therefore much heavier than air, the average weight of whose molecules is 28.955 (p. 233). It is a nonconductor of electricity, both in the gaseous and in the liquefied conditions. It is exceedingly soluble in water, so that at 10° thirty grams of water will absorb seventy grams of the gas, giving a 70 per cent solution (425 vols. : 1 Aq.). The behavior of this solution is similar to those of hydrogen chloride and hydrogen bromide (cf. pp. 211, 273). The mixture of constant boiling-point distills over at 127° (at 760 mm.), and contains 57 per cent of hydrogen iodide.

**Chemical Properties.** — Hydrogen iodide is the least stable of the hydrogen halides. When heated it begins visibly (violet color of iodine vapor) to decompose into its constituents at 180°. On account of the ease with which it parts with the hydrogen which it contains, it can be burned in oxygen gas,  $4\text{HI} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{I}_2$ . When the gas is mixed with chlorine, a violent chemical change, accompanied by a flash of light, occurs, the iodine is set free, and hydrogen chloride is produced,  $\text{Cl}_2 + 2\text{HI} \rightarrow 2\text{HCl} + \text{I}_2$ . Bromine vapor will similarly displace the iodine from hydrogen iodide.

**Chemical Properties of Hydriodic Acid HI, Aq.** — In most respects the aqueous solution behaves exactly like hydrochloric and hydrobromic acids. With oxidizing agents, for example, such as manganese dioxide, it gives free iodine, just as the others give free chlorine and bromine, respectively. Here, however, the oxidation is so much more easily carried out, that it is slowly effected by atmospheric oxygen, so that hydriodic acid left exposed to the air gradually becomes brown:  $\text{O}_2 + 4\text{HI} \rightarrow 2\text{H}_2\text{O} + 2\text{I}_2$ . The free iodine remains dissolved in the hydrogen iodide, in the form of the compound  $\text{HI}_2$ . Finally, however, the free iodine, as its quantity becomes greater, and that of the hydrogen iodide smaller, is deposited in crystalline condition. On account of the ease with which hydriodic acid parts with its hydrogen, it is frequently used in chemistry as a reducing agent.

Although the dry gas is not an acid, the solution has all the ordinary properties of this class of substances (cf. p. 117). The hydrogen

may be displaced by metals like zinc and magnesium (p. 118). The acid interacts with oxides and hydroxides, forming iodides and water (p. 213).

### FLUORINE $F_2$

The discussion of this element should logically have preceded that of chlorine, since it is of all the members of the halogen family the most active. Chlorine was taken up first, however, because its compounds are more familiar. Fluorine is found in nature chiefly in the mineral fluorite (calcium fluoride)  $CaF_2$ , in cryolite, a double fluoride of aluminium and sodium  $AlF_3 \cdot 3NaF$ , and in apatite (*q.v.*). It is found also in small amounts in bones (especially the teeth).

**Preparation.** — When a solution of hydrofluoric acid is heated with manganese dioxide, oxidation does not occur and free fluorine is not produced. Until very recently all efforts to isolate the element

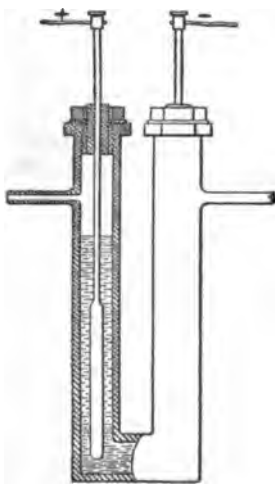


FIG. 96.

failed. It was perfectly understood that the reason of these failures lay in the greater chemical activity of fluorine, which made it more difficult of separation from any state of combination than the other halogens. Its preparation was finally achieved by Moissan (1886) by the decomposition of anhydrous hydrogen fluoride, which is liquid below  $19^\circ$ , by means of electricity. The apparatus (Fig. 96) is made of copper, which, after receiving a thin coating of the fluoride, is not further affected. To reduce the tendency to chemical union, the whole is immersed in a bath giving a temperature of  $-23^\circ$ . The electrodes are made of an alloy of platinum and iridium, which is the only substance that can resist the action of the fluorine when freshly liberated by the electric current. Hydrogen fluoride, like

other hydrogen halides, is a nonconductor of electricity, and a small quantity of potassium-hydrogen fluoride  $KHF_2$  has to be added to enable the current of electricity to pass. The fluorine is set free at the positive electrode, and hydrogen appears at the negative. The U-tube is closed after the introduction of the hydrogen fluoride by

means of blocks made of calcium fluoride, which is naturally unable further to enter into combination with fluorine. For the reception and examination of the fluorine gas, other copper tubes can be screwed on to the side necks of the apparatus, and, when necessary, small windows of calcium fluoride can be provided. It has been found that fluorine dried with extraordinary precautions is without action on clean, dry glass.

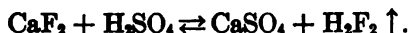
**Physical Properties.** — Fluorine is a gas whose color is like that of chlorine, but somewhat paler. Its density indicates a molecular weight of 38, showing that the molecule is diatomic (the atomic weight is 19). The gas is the most difficult of the halogens to liquefy (b.p.  $-186^{\circ}$ ).

**Chemical Properties.** — Fluorine unites with every element, with the exceptions of oxygen, chlorine, nitrogen, and the helium family, and in many cases does so with such vigor that the union begins spontaneously without the assistance of external heat. Dry platinum and gold are the elements least affected. It explodes with hydrogen at the ordinary temperature, without the assistance of sunlight. On the introduction of a drop of water into a tube of fluorine, the oxygen of the water vapor is instantly *displaced* by the fluorine, and the vessel is filled with the deep-blue gas, ozone:  $3F_2 + 3H_2O \rightarrow 3H_2F_2 + O_3$ .

The chlorine in hydrogen chloride is displaced by fluorine as easily as chlorine in turn displaces bromine or iodine.

### HYDROGEN FLUORIDE $H_2F_2$

**Preparation.** — Pure, dry hydrogen fluoride is best made by heating potassium-hydrogen fluoride,  $2KHF_2 \rightleftharpoons 2KF + H_2F_2 \uparrow$ . For ordinary purposes, however, the preparation of an aqueous solution is the ultimate object. Usually powdered calcium fluoride is treated with concentrated sulphuric acid, and the mixture distilled in a retort of platinum or lead:



The hydrofluoric acid passes over and is caught in distilled water. The aqueous solution thus obtained has to be kept in vessels made of lead, rubber, or paraffin, as glass interacts with the acid with great rapidity (see below).



**Physical Properties.** — Hydrogen fluoride is a colorless liquid, boiling at  $19.4^{\circ}$ . It mixes freely with water and, on distillation, an acid of constant boiling-point ( $120^{\circ}$  at 760 mm.) containing 35 per cent of hydrogen fluoride is obtained. The weight of 22.4 liters of the vapor varies from 51 g. at  $26^{\circ}$  to 20 g. at  $90^{\circ}$  and above. At  $90^{\circ}$  and above, therefore, the formula is HF, and at  $26^{\circ}$  the vapor is mainly a mixture of  $\text{H}_2\text{F}_2$  (40) and  $\text{H}_3\text{F}_3$  (60). Since HF is the only form which persists through a range of temperatures, we say that the substance shows **association** (see below) at lower temperatures. To keep ourselves in mind of this peculiarity, we shall use the formula  $\text{H}_2\text{F}_2$ , although the liquid undoubtedly contains many molecules which are higher multiples of HF than this.

**Association.** — Many substances resemble hydrogen fluoride in consisting of mixtures of molecules which are multiples of the simplest possible. Thus, acetic acid vapor at the boiling-point has the formula  $(\text{HCO}_2\text{CH}_3)_2$ , and sulphur vapor at high temperatures is  $\text{S}_2$  (p. 261), but at lower temperatures a mixture of  $\text{S}_2$ ,  $\text{S}_6$ , and  $\text{S}_8$ . These are **associated vapors**.

There are also **associated liquids**. Thus, sulphuric acid and nitric acid in the liquid condition are composed of more complex aggregates than  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . Even water is largely  $(\text{H}_2\text{O})_2$  or even  $(\text{H}_2\text{O})_3$ , although the vapor is  $\text{H}_2\text{O}$  (p. 202). In all such cases **dissociation** into the simpler molecules takes place *gradually* as the temperature is raised.

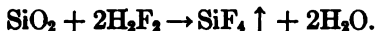
Many substances naturally possess formulæ which are multiples of the simplest without showing, as the temperature is raised, any tendency to progressive dissociation into the corresponding simplest molecules. Thus, acetylene (p. 241) is  $\text{C}_2\text{H}_2$  at all temperatures, and acetic acid (*q.v.*), although it is associated to  $\text{C}_4\text{H}_8\text{O}_4$  at its boiling-point, never becomes simpler than  $\text{C}_2\text{H}_4\text{O}_2$  at any temperature.

When a substance changes *sharply* into another substance with double or triple molecular weight, as formaldehyde  $\text{CH}_2\text{O}$ , a volatile liquid, changes into para-formaldehyde  $(\text{CH}_2\text{O})_n$ , a crystalline solid, the phenomenon is called **polymerization**.

**Chemical Properties of Hydrofluoric Acid.** — Metals like zinc and magnesium interact with hydrofluoric acid with evolution of hydrogen (p. 118). The action is less violent than with other halogen acids. The acid interacts with oxides and hydroxides, forming fluorides (p. 213). The chief difference in this respect which it ex-

hibits, when compared with the other halogen acids, is the one which leads us to assign to it the formula  $\text{H}_2\text{F}_2$ . We may displace either one or both the hydrogen atoms in the molecule with a metal. Thus, one of the commonest salts of hydrofluoric acid is potassium-hydrogen fluoride  $\text{HKF}_2$ , mentioned above,  $\text{KOH} + \text{H}_2\text{F}_2 \rightarrow \text{KHF}_2 + \text{H}_2\text{O}$ . In this respect the acid resembles sulphuric acid and other acids containing more than one replaceable hydrogen unit. Unlike the other halogen acids, hydrofluoric acid gives acid salts with great ease.

The most remarkable property of hydrofluoric acid is that it interacts readily with sand, silicon dioxide  $\text{SiO}_2$ , giving silicon tetrafluoride  $\text{SiF}_4$ , a gas, and water:



No other acid is able thus to act upon the oxide of a typical non-metallic element. In fact, in all other cases (*e.g.*,  $\text{SiCl}_4$ ), water decomposes the halide (hydrolysis), and the action goes in the opposite direction.

Glass, which is commonly made by fusing together sodium carbonate, calcium carbonate, and sand (silicon dioxide), is a mixture of silicates of calcium and sodium, and is rapidly decomposed by hydrofluoric acid. The nature of the change is shown by the two following equations:



All other silicates are decomposed according to the same plan. The silicon tetrafluoride passes off. The fluorides of calcium and sodium are solid and crumble away or dissolve. Thus the glass is completely disintegrated. The vapor of hydrofluoric acid, generated in the way described above from calcium fluoride in a lead dish, is used for etching glass. The surface of the glass is covered with paraffin to protect it from the action of the vapor, and with a sharp instrument portions of this paraffin are removed where the etching effect is desired. The vapor gives a rough surface where it encounters the glass (*test* for a fluoride). Burettes and other glass-ware are graduated in this fashion. The aqueous solution, which may also be employed, makes smooth depressions on the surface. The aqueous solution of the acid is used in the analysis of minerals containing silicates, which frequently are not attacked by other acids. It is used also for removing sand from metal castings and for cleaning the exteriors of buildings of granite and sandstone.

## THE HALOGENS AS A FAMILY

The most noticeable fact is that, if we arrange the halogens in order in respect to any one property, chemical or physical, the other properties will be found to place them in the same order. In the table, below, the sixth column contains the weight of the element in liquid or solid form dissolving in 100 c.c. of water (15°). The last column, cal. *KX*, gives the heat of formation of one gram-molecule of the potassium halide.

Element.	At. Wt.	State.	B.-p.	Color.	Sol'ty.	Cal. <i>KX</i>
Fluorine . . . . .	19.0	gas	-187°	yellow	.....	118,100
Chlorine . . . . .	35.5	gas	- 34	yellow	.....	104,300
Bromine . . . . .	79.9	liq.	+ 59	brown	3.22	95,100
Iodine . . . . .	126.9	solid	+184°	violet	0.015	80,100

It will be seen that, as the atomic weight (chem. prop.) increases, the boiling-point (b.-p.) rises, the color deepens and passes towards the blue end of the spectrum, the solubility diminishes (phys. props.), and the heat of union with potassium (chem. prop.) becomes smaller. The vigor with which the halogens unite with hydrogen and the metals is greatest with fluorine and diminishes progressively until we reach iodine. We shall see later that the affinity for oxygen, on the other hand, *increases* as we pass from fluorine to iodine.

Although showing different degrees of activity, the halogens are closely alike in chemical nature. That is, **the relations** (p. 226) they show when in combination are similar. When united with hydrogen and the metals, they are all *univalent*. In their oxygen compounds, however, they exhibit a higher valence. Their oxides interact with water to give acids, and they are therefore non-metals (p. 150). They are strongly electro-negative (pp. 213, 269), as non-metals all are. Their hydrides, when dissolved in water, are all active acids. This, and their valence, distinguish the halogen family from other groups of non-metals. Thus, oxygen and sulphur are bivalent (and the latter sexivalent also), and the hydrides of oxygen ( $H_2O$  and  $H_2O_2$ ) and of sulphur ( $H_2S$ ) are very feeble acids.

**Order of Activity of the Non-Metals.** — The way in which chlorine displaces bromine and iodine from bromides (p. 273) and iodides (p. 276), and bromine, in turn, displaces iodine suggests an

order of activity for non-metals. It was noted that oxygen displaced iodine from hydriodic acid (p. 279) and that iodine displaced sulphur from hydrogen sulphide (and all other sulphides). The order is, therefore, F, Cl, Br, O, I, S.

#### COMPOUNDS OF THE HALOGENS WITH EACH OTHER

Iodine unites with chlorine to form two compounds. The most familiar is a red crystalline substance **iodine monochloride**  $\text{ICl}$ . The **trichloride**  $\text{ICl}_3$  is made by the use of excess of chlorine. Iodine unites with bromine to form the compound  $\text{IBr}$ , while a compound with fluorine  $\text{IF}_3$ , is supposed to exist. None of these compounds is particularly stable, and some of them decompose very easily.

It is frequently stated that elements which resemble one another chemically show little tendency to chemical union. Yet in the case of  $\text{IBr}$ , for example, the tendency to decompose into the elements ( $2\text{IBr} \rightarrow \text{I}_2 + \text{Br}_2$ ) must be interpreted as meaning that the iodine and bromine prefer to unite with themselves to form the molecules  $\text{I}_2$  and  $\text{Br}_2$  rather than with one another. In view of this the above remark loses some of its point, for an element certainly resembles itself more than it does any other, and the compounds  $\text{Cl}_2$ ,  $\text{H}_2$ , etc., are amongst the most stable that we know.

**Exercises.** — 1. What impurities is commercial iodine likely to contain? In what way does heating with potassium iodide (p. 275) free it from these?

2. Classify all the chemical actions in this chapter according as they belong to one or other of the ten kinds (p. 228).

3. What are the relative volumes of the gases in the interaction of chlorine with hydrogen bromide (p. 273), and hydrogen iodide (p. 279), respectively?

4. Tabulate, more fully and specifically than is done in the section on "The Halogens as a Family," (a) the physical properties, (b) the chemical properties, (c) the chemical relations, of the members of this group.

5. Construct the equation on p. 275 by the use of partial equations as in the example on p. 270.

6. Using the method given on p. 270, construct a single equation for the formation of iodine, water, and hydrogen sulphide directly from potassium iodide and sulphuric acid.

7. What are the relative volumes of the gases in the action of,

(a) fluorine and water vapor (p. 281), (b) chlorine and iodine vapors in forming the monochloride and (c) the trichloride.

8. In the French process for liberating iodine (p. 275), why must excess of chlorine be avoided?

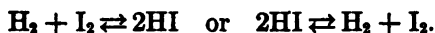
9. In liberating bromine from the mother-liquor (p. 269), why must excess of sulphuric acid and manganese dioxide be avoided?

## CHAPTER XV

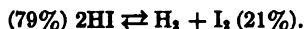
### CHEMICAL EQUILIBRIUM

IN spite of its formidable title, this chapter will introduce nothing novel. Its purpose is to collect together and organize more definitely a number of scattered facts and ideas which have already come up in various connections. On this account, however, it will be all the more necessary for the reader to refresh his remembrance of these facts and ideas by re-reading all pages to which reference is made.

**Reversible Actions.** — In discussing the union of hydrogen and iodine (p. 277), it was stated that the progress of the action ceases while yet a large amount (21 per cent at  $445^{\circ}$ ) of *both* the substances necessary for its maintenance still remains available. Now the materials left over are presumably no less capable of uniting than the parts which have already united. The solution of this mystery lies in the fact (p. 279) that *decomposition of the compound* can begin at  $180^{\circ}$ , and therefore takes place actively at  $445^{\circ}$ . Hence the product of the union must begin to dissociate, in part at least, as soon as any of it is formed. Thus two changes, one of which undoes the work of the other, must go on simultaneously. In consequence of this, neither can reach completion. As we should expect, experiment shows that it makes no difference whether we start with pure hydrogen iodide or with a mixture of pure hydrogen and iodine: the proportions of the three materials found in the tube, after it has been heated for a sufficient length of time, are in both cases the same. A **general statement** may be founded on facts like this, to the effect that a **chemical action must remain more or less incomplete when the reverse action also takes place under the same conditions** (*cf.* p. 40). Two arrows pointing in opposite directions are used in equations representing reversible changes:



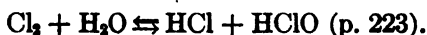
It will be observed that representing reversible actions by equations involves a departure from the original meaning of an equation. Thus at  $445^{\circ}$ , 79 per cent of the substances are in the form HI and 21 per cent in the uncombined state:



In other words, the amounts of matter on the two sides are *not equal*. Each side, taken separately, shows correctly the *proportions* used in the interaction for which it stands, however. Hence the equation in a reversible action professes to show quantitatively the change which *would occur* if each of the two opposed actions it includes were to be allowed separately to proceed to completion.

The following are examples of actions of the exactly same kind. They should now be looked up and studied attentively. The discussion in the following sections, for which they furnish the basis, cannot otherwise be understood: (1) The interaction of chlorine and water (p. 223), which was fully discussed at the time; (2) the behavior of iodine vapor (p. 261), of water vapor (p. 148), of sulphur vapor (p. 261), of phosphorus vapor (p. 261); (3) the behavior of phosphorus pentachloride vapor (p. 260); (4) Deacon's reaction (p. 217). Examples of this kind are called **homogeneous systems**, because all the interacting substances are either gaseous or in solution ( $\text{Cl}_2 + \text{H}_2\text{O}$ ).

When the action is one which is reversible, but, under the circumstances being discussed, proceeds farther towards completion in one direction than in the other, the arrow will be modified to indicate this fact:



When this relative completeness is due to volatilization or precipitation, the fact will be indicated by vertical arrows:



Cases in which a gas or a solid separates are called **heterogeneous systems**.

**Actions which Proceed to Completion.**—All chemical actions do not belong to the reversible, incomplete class. Many proceed uninterruptedly to exhaustion of one, or all, of the ingredients. For example, equivalent amounts of magnesium and oxygen combine completely:  $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$ . Here, however, the product is not decomposed even at the white heat produced by the vigor of the union. Indeed, magnesium oxide cannot be decomposed, and the action reversed, at any temperature we can command. The other **complete actions**, like the decomposition of potassium chlorate (p. 83), are so because they are likewise irreversible.

**Kinetic-Molecular Explanation.** — Restating these facts in terms of molecules will enable us to reason more clearly about this variety of chemical change. Suppose we start with the materials represented on *one side* only of such an equation say the hydrogen and iodine in that on p. 287. The molecules of these materials will encounter one another frequently in the course of their movements. In a certain proportion of these collisions the chemical change will take place. In the earliest stages there will be few of the new kind of molecules (say, hydrogen iodide), but, as the action goes on, these will increase in number. There will be two consequences of this. In the first place the parent materials (in this case, hydrogen and iodine) will diminish in amount, the collisions between their molecules will become fewer, and the speed of the forward action will therefore become less and less. In the second place the increase in the number of molecules of the product (hydrogen iodide) will result in more frequent collisions between them, in more frequent occurrence of the chemical change which they can undergo, and thus in an increase in the speed of the reverse action. The forward action begins at its maximum and decreases in speed progressively; the reverse action begins at zero and increases in speed. Finally the two speeds *must become equal*, and at that point perceptible change in the condition of the whole must cease (*cf.* pp. 169-170).

The most immediate inference from this mode of viewing the matter is, that the apparent halt in the progress of the action does not indicate any cessation of either chemical change. Both changes must go on, in consequence of the continued encounters of the proper molecules. But since the two changes proceed with *equal speeds* they produce no alteration in the mass as a whole. In fact, the final state is one of equilibrium, and not of repose. Hence, chemical changes which are reversible lead to that condition of seemingly suspended action which we speak of as **chemical equilibrium**.

**Chemical Equilibrium and its Characteristics.** — The detailed discussions of the relations of liquid and vapor (pp. 145, 169-170), of ice and water (p. 144), of saturated solution and undissolved solid (pp. 185, 192-195), and of a gas dissolving in a liquid (p. 187), have already familiarized us with the term equilibrium and its significance. We can, in fact, apply to the discussion of any kind of reversible phenomena, the sets of ideas in regard to exchanges of molecules there elaborated.

In particular, the reader will note that the **three characteristics** of



a state of equilibrium, developed and illustrated in the case of the physical equilibrium between a liquid and its vapor (p. 169), apply also to a typical case of chemical equilibrium, such as that now before us. Thus:

1. There are the two opposing tendencies, which ultimately balance one another. Here they are the tendency of the hydrogen and iodine to produce hydrogen iodide, and the tendency of the hydrogen iodide to reproduce hydrogen and iodine by this interaction. In other words, they are the **apparent activity** of the hydrogen iodide reaction, and the **apparent activity** \* of the hydrogen and iodine interaction.

2. At equilibrium the two opposing tendencies or activities are still in full operation, although their effects then neutralize one another.

3 (and this is the chief mark of chemical, as it is of physical equilibrium). The system is in a sensitive state, so that a change in the conditions (temperature and partial pressure or concentration), even if slight, produces a corresponding change in the state of the system, and does this by favoring or disfavoring one of the two opposing tendencies or apparent activities. Such a change is called a **displacement of the equilibrium**, for the system settles down in a new state of equilibrium with new proportions of the two sets of substances, corresponding to the changed conditions. Thus, in the present instance, a change from  $445^{\circ}$ , where there is 79 per cent of the material in the form of hydrogen iodide, to  $508^{\circ}$  results in the diminution of this proportion to 76 per cent. The equilibrium is affected by changes in concentration also, as we shall presently see (pp. 291-293).

Now, the foregoing facts show that the key to understanding chemical activities, their magnitudes, their changes, and especially their practical results, *must lie in knowing how changes in the conditions affect them*. Hence, to the chemist, familiarity with the influence of conditions on chemical phenomena must be of the greatest practical importance. We therefore address ourselves to the discussion of this subject.

The "conditions" to be considered are familiar — temperature, and concentration or, in the case of a gas, partial pressure. The "activity" of an action is accurately measured by the speed with

\* We use the term "apparent activity" for the activity as we see it. In the same action it varies with the conditions. The **intrinsic activity** or **affinity**, on the other hand, is the absolute activity of the action under certain carefully defined conditions (see p. 295), which are the same for all actions to be compared.

which the action proceeds. Thus, if the foregoing section be re-examined, it will be seen that we spoke throughout of the *speed*, rather than of the tendency or activity.

Finally, temperature and other conditions influence also the activities in, and therefore the speeds of, those actions which proceed to completion, and are not reversible. Hence, unless our statements are expressly restricted to reversible actions and to states of equilibrium, they apply to all chemical changes.

**The Influence of Concentration.** — In the first place, let us assume that the temperature is constant, and let us confine our attention for the present to the influence of concentration upon a chemical reaction. We have seen (p. 289) that the speed of a chemical change is determined by the frequency with which the molecules of the interacting substances encounter one another. The frequency of the encounters amongst a given set of molecules, resulting in a definite chemical change, will in turn evidently depend entirely upon the degree to which the molecules are concentrated in each other's neighborhood. Larger amounts of one of the materials, for example, will not result in more rapid chemical action in the sense which this material favors, if the larger amount of material is also scattered through a larger space. Chemical changes, therefore, are not accelerated by increasing the mere quantity of any ingredient, but only by increasing the **concentration of its molecules**. Thus, a large amount of hydrochloric acid with a piece of zinc will generate hydrogen no faster than a smaller amount. But substitution of more concentrated acid will instantly increase the speed of the action. In the second case, the number of molecules of the acid reaching the zinc per second is greater, and this action, being non-reversible, proceeds more rapidly to complete consumption of the zinc. So also, iron burns faster in oxygen (100 per cent) than in air (20 per cent oxygen).

With a reversible action the effect on the speed is the same, excepting that the continued activity of the reverse action prevents the direct one from reaching completion. Thus, if, in the action of hydrogen upon iodine, we introduce *into the same space* an extra amount of hydrogen, this facilitates the formation of hydrogen iodide by increasing the possibilities of encounter between hydrogen and iodine, while at the same time it does not affect (*cf.* p. 111) the number of encounters in a given time between hydrogen iodide molecules which result in the reverse transformation. The proportion of hydrogen iodide formed, therefore, from a given amount of iodine will be

greater, although the total possible (by complete consumption of the materials) has not been altered, since the quantity of one ingredient only has been increased. The introduction of an excess of iodine would have had precisely the same effect.

**An Experimental Illustration.**—It is easy to illustrate this experimentally. A reaction in which the effects of different concentrations were carefully studied by Gladstone (1855) affords a good example. If ferric chloride and ammonium thiocyanate are mixed in aqueous solution, a liquid containing the soluble, *blood-red* ferric thiocyanate is produced. The compound radicals are  $\text{NH}_4$  and  $\text{CNS}$ , and the action is a simple double decomposition:



The action is a reversible one, and the system is homogeneous, *i.e.*, there is no precipitation. Now, if the two just-named salts are mixed in very dilute solution in the proportions required by the equation, say by adding 20 c.c. of a deci-normal solution (p. 182) of each to several liters of water, a pale-reddish solution is obtained. When this is divided into four parts, and one is kept for reference, the addition of a little of a concentrated solution of ferric chloride to one jar, and of ammonium thiocyanate to another, will be found to deepen the color by producing more of the ferric thiocyanate. On the other hand, mixing a few drops of concentrated ammonium chloride solution with the fourth portion will be found to remove the color almost entirely on account of its influence in accelerating the backward change.

**The Law of Molecular Concentration.**—The general principle discussed and illustrated in this section may be called the **law of molecular concentration**, and may be stated as follows: **In any given chemical change the apparent activity, and therefore the speed of that change is proportional to the molecular concentration of each interacting substance.** This holds whether the action is reversible or not.

Of course, when *different* actions are compared, the **intrinsic affinities** will be different, and so, with equal molecular concentrations, the speeds will be different. In the same action, a change in **temperature** (see p. 304) will alter the speed.

The phrase “active mass” is commonly employed instead of the words “molecular concentration.” It is distinctly misleading, however, for, as we have

seen, it is not on the mass of a substance, but on the quantity of it in a given volume, that the speed of the action depends. If a physicist spoke of the mass, when he meant density (quantity in a given volume), he would lose all scientific standing at once. But in chemistry it is not considered bad form to use the word mass in this connection, although a conception of the nature of density is intended. Some kinds of nomenclature are used more loosely in chemistry than they would be in any other science (p. 210).

The following is a more exact statement of the law of molecular concentration than that given above: The speed of a given chemical change is proportional to the first, or some higher power of the molecular concentration of each interacting substance, the power being for each substance determined by the number of molecules of that substance concurring in the interaction [or by the order of the action into which its molecules enter, or by the number of its molecules appearing in a molecular equation representing the action], the "action" in question being the *slowest* of the partial actions involved, when the action, as a whole, is achieved through consecutive partial actions (see p. 296).

**A Warning.** — The reader must avoid the idea that a reversible action is one which goes to completion, and then runs back to a certain extent. This conception would be contrary to the fact, and opposed to the principles of energetics, as well as inexplicable by the kinetic-molecular view.

This erroneous idea seems to assume that a chemical action has momentum, which is not the case. If a reaction did have momentum, and ran first to completion, then, on reversal, it would have the same momentum and would come back to the starting point (the original substances). There would be no more reason for its stopping at an intermediate position on the return, than on the forward journey. In fact, somewhat like a pendulum (which *does* have momentum), it would swing back and forth and never come to rest, or rather to a state of balanced activities! A pendulum, when pulled out of the vertical position, starts with no speed, then gains a little, and finally moves with its greatest velocity when passing through the vertical position. But a chemical reaction does just the opposite. The forward action starts at its maximum speed (because the interacting molecules are at a maximum, since none have been used up) and goes more and more slowly until, partly because the interacting molecules are fewer, and partly because the reverse action is increasing and undoing its work, the action can produce no further change and the equilibrium point is reached. This is the molecular view of this fallacy.

In the point of view of energy, the action proceeds at first because the free energy in the system is diminishing. At the equilibrium

point, there is also an energy equilibrium, and the energy of the system neither diminishes nor increases. To carry the action beyond the equilibrium point, however, would require an increase, from some outside source, in the energy of the system.

As to the facts, a system involving a reversible action changes in composition while approaching equilibrium, but when it has reached that point, no further changes, such as the pendulum analogy suggests can be detected. To be specific, if the ferric chloride and ammonium thiocyanate reaction, described above, first went to completion, and then receded to an equilibrium position, the mixture would first become deep red, and then go back to a paler color, but no such phenomenon has ever been observed.

***Formulation of the Relation between Molecular Concentration and Speed of Reaction.*** — These principles will become clearer when stated in somewhat more precise terms. We confine our attention to homogeneous systems, in the first place.

The molecular concentration is stated, numerically, for each substance, in terms of the number (whole or fractional) of moles (gram-molecular weights, p. 236) of the substance contained in a liter of the whole mixture. There is the same number of molecules in a mole of every substance, namely, the number of molecules in 32 g. of oxygen (*cf.* p. 238). Hence the number of moles per liter defines the concentration of the substances in terms of this number of molecules in a liter as the unit of concentration.

Thus, in a solution containing 25.4 g. of free iodine ( $\frac{1}{10}$  of a formula weight,  $I_2$ ) per liter, the solution is 0.1 molar (p. 183), and the molecular concentration of the iodine is 0.1. When the substance is a gas, the concentration of the molecules is proportional to the partial pressure of the gas. Now, one mole of a gas occupies 22.4 liters at one atmosphere pressure (and  $0^\circ$ ). Hence, when one mole of a gas is contained in 1 liter, and its molecular concentration is therefore 1, it exercises 22.4 atmospheres partial pressure. When the partial pressure of one gas in a mixture is two atmospheres, its molecular concentration is  $\frac{2}{22.4}$  or 0.09.

The speed of the action is also expressed, numerically, in moles of each substance transformed per minute or, for slow reactions, per hour.

Using these units, the relation between the molar concentrations and the speed is easily expressed. The speed is proportional to the molar concentration of each molecule appearing in the molecular

equation for the action, and to the intrinsic affinity or activity of the action. For example, in the interaction of hydrogen and iodine (p. 287),  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ , if  $[\text{H}_2]$  and  $[\text{I}_2]$  represent the molar concentrations, which can be varied, and  $k$  is a constant, representing the affinity, which is invariable for each action, and  $S$  is the speed, then:

$$[\text{H}_2] \times [\text{I}_2] \times k_1 = S.$$

Similarly, for the reverse action:  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ :

$$[\text{HI}] \times [\text{HI}] \times k_2 = [\text{HI}]^2 \times k_2 = S.$$

Note that  $[\text{HI}]$  represents the *total* concentration of HI (not one-half of it), because *every* molecule of HI present may play the part of either one of the two demanded by the equation.

It need hardly be added that, clearly, when the concentration of any ingredient becomes zero (say by all of it entering into combination), or when the affinity is zero, the speed  $S$  must become zero, that is to say, no action takes place.

The **affinity** or **activity** ( $k$ ) is always represented numerically by the speed in moles per unit of time when the molar concentration of each ingredient is unity (see next section).

**More Specific Formulation of Speed of Reaction.**—In the preceding section attention was not called to one practical difficulty. Since, as the action proceeds, the materials are being used up, their concentrations do not remain constant, but *progressively diminish* during the period of observation (1 minute or 1 hour). Thus, the action becomes, on this account, slower and slower.  $S$ , therefore, as used above, is the speed at a given moment. If applied to one minute (or one hour), it is the amount which *would* be transformed if the concentrations present at that moment were artificially maintained during the whole minute (or hour).

Now, the theoretical speed at constant concentration, used in the above formulae, can be calculated from the speeds *observed* with diminishing concentrations. It will be noted that when the concentrations are unity,  $[\text{H}_2] = [\text{I}_2] = 1$ , and therefore  $1 \times 1 \times k = S$ . That is, with unit concentrations,  $k = S$ . The plan, therefore, is to experiment with different concentrations at the same temperature, and to measure the amounts transformed in measured times in each case. We can then calculate (see below) from the data of each set the speed (moles transformed per hour or minute) which would be shown by constantly maintained unit concentrations of the materials. The answers are the values of  $k$  for unit concentrations, based upon measurements with different concentrations of the same substances, and they agree closely with one another. The values of  $k$  for several different chemical actions, however, may differ widely, and are measures of the relative activity of each.

The relation of the theoretical speed with *constant unit concentration* to that which is *observed* with diminishing concentration is as follows: For an action of the form:  $A \rightarrow B + C$ , where the change in only one molecule constitutes the action, if  $[A]$  is the initial molecular concentration of  $A$ , and  $x$  is the fraction of this which is transformed in the time  $t$ ,

$$k = S_{\text{unit concn.}} = \log_e \frac{[A]}{[A] - x} + t.$$

When two molecules have to interact:  $A + B \rightarrow C + D$ , the formula is still more complex. If the substances are present in equivalent proportions, their molecular concentrations in this special case are alike, and may each be represented by  $[A]$ , for  $[A] = [B]$ . The relation is then:

$$k = S_{\text{unit concn.}} = \frac{x}{[A]([A] - x)} + t.$$

The mathematical derivation of these relations will be found in any work on physical chemistry.

**An Illustration.** — The following illustration (see also Sulphurous acid) will make all this clearer. When arsine  $\text{AsH}_3$  (*q.v.*) is heated at  $310^\circ$ , it decomposes gradually into hydrogen and arsenic:



The action is not appreciably reversible. The arsenic assumes the solid form. The gas is inclosed in a tube which is kept in a bath at  $310^\circ$ , and a manometer shows changes in pressure. Since, as the action proceeds,  $1\frac{1}{2}$  molecules of hydrogen take the place of each molecule of arsine, the total pressure slowly increases. Every increase of 1 mm. in the pressure is the result, therefore, of an addition of 3 mm. partial pressure of hydrogen and a reduction of 2 mm. in the partial pressure of the arsine. The molecular concentrations are proportional to the pressures, and change, therefore, in the same ratios. The observations (first two

\* Ordinarily we should write the equation  $2\text{AsH}_3 \rightarrow 2\text{As} + 3\text{H}_2$ . But this form would make the speed proportional to  $[\text{AsH}_3]^2$  and calculation would then give us inconstant values for  $S$ . The reason for this apparent irregularity is that the action takes place in two stages (consecutive reactions, p. 272). First  $\text{AsH}_3$  decomposes to give  $\text{As} + 3\text{H}$ . Then the atoms of hydrogen combine in pairs to form  $\text{H}_2$ . The latter of these actions, however, is very speedy, while the former is the one that takes time, and it is the time occupied by the former alone that we are measuring. Hence, only the former is involved in the calculation. This point is covered by the last part of the more exact statement of the law of molecular concentration (p. 293). The rates of very fast actions cannot be measured. In a sense, it is the *slowness* of the action, that is, the time required for a certain amount of chemical change, that we are measuring when we determine so-called speeds of reaction.

columns), together with the data deduced from the first two by calculation, were as follows:

TIME, HOURS.	PRESS., MM.	MOLECULAR CONCENTRATIONS.		S PER HOUR.
		Total.	AsH <sub>3</sub> Transfmd.	
0	784.84	0.02159		
3	878.50	0.02416	0.00514	0.0906
4	904.05	.....	.....	.....
8	987.19	.....	.....	.....

We must first ascertain the molecular concentration of the arsine corresponding to the observed pressure at the beginning. We remember that at 22.4 atmospheres, or  $22.4 \times 760$  mm. and  $0^\circ$ , the molar concentration of a gas has the value 1 (p. 294). The actual initial pressure 784.84 mm. at  $310^\circ$  would become, at  $0^\circ$ ,  $\frac{784.84 \times 273}{(310 + 273)}$ , or 367.5 mm. The molecular concentration is here, therefore,  $\frac{367.5}{22.4 \times 760}$  or 0.02159 moles per liter. After 3 hours, some hydrogen has been formed. The pressure has increased to 878.50 mm. Reducing as before, this represents a molecular concentration of all ingredients of 0.02416 moles per liter. The increase is 0.00257. This, as was demonstrated above, corresponds to a loss of  $2 \times 0.00257$ , or 0.00514 moles per liter of arsine. Now, employing the formula given above, we find the speed per hour:

$$k = S_{\text{unit concn.}} = \log_e \frac{[\text{AsH}_3]}{[\text{AsH}_3] - x} + t = \log_e \frac{0.02159}{0.01645} + 3 = 0.0906.$$

This result means that, if the concentration of the arsine were to be maintained at the initial value by continual renewal of the waste, then 0.0906 (9.06 per cent) of the initial amount would be decomposed in an hour. Using the pressures at 4 and at 8 hours, the reader will obtain by calculation, practically the same value for  $k$ . Other experiments with still different concentrations, provided the temperature was the same (p. 291), would likewise give the same results, for this is the speed calculated back to unit concentration. Thus the affinity or activity of the action may be measured with any concentration, and expressed in moles transformed per hour with unit concentration. Similar measurements with other actions then enable comparisons of their relative activities to be made (see Exercise 10, end of this chapter).

### *Formulation of the Conditions for Chemical Equilibrium.*

— The plan outlined above (p. 295) may be used further to formulate the conditions for chemical equilibrium. As we have seen (p. 289),



a characteristic of a system in chemical equilibrium is that the speeds of the forward and reverse actions have become equal. If, then,  $[H_2]_{eqm.}$ ,  $[I_2]_{eqm.}$ , and  $[HI]_{eqm.}$ , now represent the molecular concentrations when the system *has reached equilibrium*, then, since the speeds are equal:

$$[H_2]_{eqm.} \times [I_2]_{eqm.} \times k_1 = [HI]^2_{eqm.} \times k_2$$

and

$$\frac{[H_2]_{eqm.} \times [I_2]_{eqm.}}{[HI]^2_{eqm.}} = \frac{k_2}{k_1} = \text{constant} = K.$$

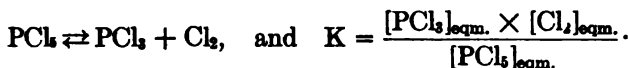
In words, this means that if we change the amount of hydrogen iodide placed in the same vessel, or if we use amounts of hydrogen and iodine which are not equivalent, the numerical value at equilibrium of each concentration ( $[H_2]$ , etc.), will, of course, be different, but the product of the concentrations of hydrogen and of iodine, divided by the concentration of the hydrogen iodide, will always give the same numerical value for the constant at the same temperature. This numerical value is called the **equilibrium constant**.

If, for example, the value of the constant is  $\frac{1}{4}$ , then the speeds of the two actions, if each were to proceed unimpeded (say in separate vessels) with constantly maintained unit concentrations of the materials, would be in the ratio  $k_2 : k_1$  or  $1 : 4$ . From this it will be seen that measurement of the concentrations present in a system which has reached equilibrium gives us the data for calculating the value of this ratio. In other words, it gives us the means of ascertaining the relative magnitudes of the intrinsic affinities of the opposed actions.

Applying this to the data given (p. 290) for hydrogen iodide, at  $445^\circ$ , with equivalent quantities of the two elements, nearly 0.8 (more exactly, 79 per cent) of the weight of each is in the form HI, and 0.2 in the mixture  $H_2 + I_2$ . Thus in every 100 molecules, 80 are HI, 10 are  $H_2$ , and 10 are  $I_2$ . Thus  $K = 0.1^2 \div 0.8^2 = \frac{1}{64}$ . That is to say, the union of hydrogen and iodine would take place with 64 times as great a speed as the dissociation of hydrogen iodide if each action could proceed without reversal and under identical conditions. Or, in terms of the kinetic theory, the collisions of the  $H_2$  and  $I_2$  molecules result many times more often in chemical change than do collisions of HI molecules.

The case of hydrogen iodide is comparatively simple because the volume is not altered by the progress of the action (see below). The

expansion when phosphorus pentachloride (p. 260) dissociates compels us to take account of the volume. The equation is:



If one gram molecule of the pure  $\text{PCl}_5$  is taken, and  $x$  is the proportion dissociated, and  $v$  the volume occupied by the whole, then  $[\text{PCl}_5]_{\text{eqm.}} = [\text{Cl}_2]_{\text{eqm.}} = \frac{x}{v}$ , and  $[\text{PCl}_3]_{\text{eqm.}} = \frac{1-x}{v}$ . Thus  $K = \frac{x^2}{(1-x)v}$ . Now at  $250^\circ$  (and 760 mm.), for example, 0.8 of the whole weight of material is dissociated:  $x = 0.8$  and  $1-x = 0.2$ . Hence  $K = 0.8^2 \div 0.2v = 3.2 \div v$ . To obtain the value of  $v$  we note that a gram molecule at 760 mm. and  $0^\circ$  occupies 22.4 liters. At  $250^\circ$  it occupies  $22.4 \times (250 + 273) \div 273$  l. But *this* mass of gas contains 0.8 more molecules because of dissociation, and its volume is, therefore,  $1.8 \times 22.4 (250 + 273) \div 273 = v = 77.2$  l. Thus  $K = 3.2 \div 77.2 = \frac{1}{25}$ . Otherwise stated, the union of the trichloride and chlorine would proceed twenty-five times as fast as the dissociation, if each of the three substances was present in unit concentration, and each action could proceed independently without reversal.

### *The Effect of Changes of Volume on Chemical Equilibrium.*

— Our applications of the theory of equilibrium will be chiefly to dissolved bodies, and hence the effect on the equilibrium point of changes in volume (by dilution or the reverse) will require frequent consideration. Now dilution, for example, diminishes opportunities for encounters between the substances on both sides of the equation. In the second of the above illustrations, increasing the volume decreases the rate at which the chlorine and the phosphorus trichloride can combine. Since, however, the speed of the dissociation depends on the state of the  $\text{PCl}_5$  molecules only, and is unaffected by their nearness to or remoteness from one another, the forward action will not be weakened at all. Hence, dilution increases the degree of dissociation. In general, change in volume will affect the equilibrium point whenever there are more molecules on one side of the equation than on the other.

In mathematical terms, when we change the volume to  $\frac{1}{n}$  times its former value ( $n$  whole or fractional), the concentration changes  $n$  times. The equation for equilibrium then becomes, momentarily,

$n [\text{PCl}_3] \times n [\text{Cl}_2] \div n [\text{PCl}_5] \neq K$ , or  $n [\text{PCl}_3] \times [\text{Cl}_2] \div [\text{PCl}_5] \neq K$ . To restore the value of the expression to equality with  $K$ , change must occur in the concentrations  $[\text{PCl}_3]$ ,  $[\text{Cl}_2]$ , and  $[\text{PCl}_5]$ . When  $n$  is  $< 1$ , that is, when the volume increases, some  $\text{PCl}_5$  must pass into the form  $\text{PCl}_3$  and  $\text{Cl}_2$  until  $[\text{PCl}_3] \times [\text{Cl}_2] \div [\text{PCl}_5] = K$ , as before. That is, dilution increases the degree of dissociation.

In case of hydrogen iodide, and in all others where the number of molecules taking part in the direct and reverse actions is the same, change in the volume of the system has no effect on the position of the equilibrium point. Thus dilution diminishes the chance of encounter between two HI molecules to the same extent that it interferes with encounters between  $\text{H}_2$  and  $\text{I}_2$  molecules. Conversely, increase in all concentrations, by diminution of volume, favors both actions equally. Hence, at  $445^\circ$ , 79 per cent of HI will always be present at last, whatever the volume occupied by a given amount of the materials. In mathematical terms, if we diminish the volume  $n$  times ( $n$  whole or fractional), we increase the concentration of each constituent  $n$  times. The values become  $n [\text{H}_2]$ ,  $n [\text{I}_2]$ , and  $n [\text{HI}]$  respectively:

$$\text{and} \quad K = \frac{n^2 [\text{H}_2] \times [\text{I}_2]}{n^2 [\text{HI}]^2} = \frac{[\text{H}_2] \times [\text{I}_2]}{[\text{HI}]^2}.$$

**Heterogeneous Equilibrium.** — A modification of the above conceptions is necessary when the mixture is not homogeneous. If, for example, one of the constituents is present as a solid or a gas, in greater amount than can be dissolved by the liquid in which alone the chemical change takes place, then, according to the definition of saturated solution (p. 192), the concentration of the dissolved material will be constant at a given temperature as long as physical equilibrium between the solid and the solution is maintained. This is a case especially likely to occur when slightly soluble (so-called "insoluble") bodies (*cf.* p. 179) are concerned.

The same reasoning applies also to very slightly volatile solids. The concentration of the vapor of a solid body present in excess (measured by its vapor pressure) will be constant so long as the temperature is fixed, and interaction with a superincumbent gas will take place chiefly through the vapor.

In both these cases the concentrations of the active parts of the slightly soluble and slightly volatile bodies, respectively, are not subject to variation — they are constant. Thus, with the action,



the concentrations of the vapors  $[\text{CuSO}_4 \cdot \text{H}_2\text{O}]$  and  $[\text{CuSO}_4]$  are con-

stant, and utterly negligible and that of water  $[H_2O]$  alone is subject to alteration. We have, therefore,

$$\frac{[CuSO_4] \times [H_2O]}{[CuSO_4 \cdot H_2O]} = K, \text{ or } [H_2O] = \frac{[CuSO_4 \cdot H_2O]}{[CuSO_4]} K$$

in which, since  $[CuSO_4 \cdot H_2O]$ ,  $[CuSO_4]$ , and  $K$  are constant,  $[H_2O]$  must be constant also. But the pressure of a gas is proportional to its molecular concentration, according to Avogadro's hypothesis. Therefore, in this action, the pressure of the water vapor (the **dissociation pressure**) should be constant irrespective of the extent to which the dissociation has progressed. Observation shows that this is the case. All hydrates, as we have seen (pp. 151-154), behave in a precisely similar way, and furnish numberless confirmations of this application of the law of molecular concentration.

**Applications: The Reverse Action. Displacement of Equilibria.** — Of special interest to the chemist are the conditions under which the equilibrium point may be displaced and more nearly complete realization of one of the two opposed changes may be brought about.

We have seen (p. 292) that one way in which a reversible action may be forced nearer to completion in one direction or the other is the introduction of an excess of one of the ingredients contributing to the action. This method of displacing the equilibrium point, however, cannot be very effective unless it is possible to introduce an exceedingly large excess of the selected ingredient in a high degree of molecular concentration, since this operation *does not in any way effect or, in particular, restrain the reverse action* which is continually undoing the work of the forward one. A much more effective means of furthering the desired direction of such actions is found, therefore, in the restraint or practical annulment of the reverse action. A good way to accomplish this is to allow the products of the direct action to separate into an inhomogeneous mixture. Any agency which could remove the free iodine as fast as it was formed in the decomposition of hydrogen iodide, for example, would entirely stop the reproduction of the compound and so would enable the dissociation  $2HI \rightleftharpoons H_2 + I_2$  to run to completion. The concentration of one product can often be reduced practically to zero. To achieve the same effect by *adding* an interacting substance, the concentration of the latter would have to be raised to infinity, which is impossible.

This might be realized\* by causing one end of a sealed tube charged with hydrogen and iodine, after the contents had settled down to a condition of equilibrium, to project from the bath in which the whole had been kept at  $445^{\circ}$  (Fig. 97, which is simply diagrammatic).

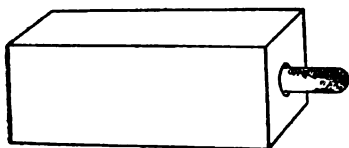


FIG. 97.

By cooling this end, a large part of the 21 per cent of free iodine would quickly be condensed in it to the solid form, while the hydrogen would remain gaseous. Only the trace of vapor which cold iodine gives would then be available to interact with the hydrogen and reproduce hydrogen iodide. Meanwhile the decomposition of the latter would go on, and thus, eventually, almost all the iodine would be found free in one end of the tube, and the hydrogen, all free likewise, would occupy the rest. By this purely mechanical adjustment the chemical change would in this way be carried from 21 per cent completion to almost absolute completion



If, on the other hand, arrangements were made to have powdered marble, in a sealed bulb of thin glass, enclosed in the tube, we might imagine the very opposite effect of the above to be produced. The breaking of the bulb of marble, when equilibrium had been reached would provide means for the removal of all the hydrogen iodide, while the hydrogen and iodine would still be gaseous. Thus, the compound having been removed, there would be no reverse action to compensate for the union of the elements. The whole material would therefore, soon have passed through the form HI. Hence, by another mechanical arrangement, an action which ordinarily could progress to only 79 per cent would be turned into a complete one.

The discussion of hydrogen iodide in this chapter shows very clearly why we do not prepare the compound by uniting the elements (p. 277). (1) Since the elements interact as gases, very bulky apparatus would be required to prepare any considerable quantity; (2) the

\* For another illustration, see under Ammonia.

† The hydrogen iodide would be destroyed by interaction with the marble



The calcium iodide is a solid. The two gases, carbon dioxide and water vapor do not interact with hydrogen or with iodine, and would not, therefore, interfere with the formation of fresh hydrogen iodide.

union is very slow, taking many hours at  $283^{\circ}$  to give 82 per cent; (3) it is incomplete, at best, and we obtain a mixture, and not a pure substance.

***Reversibility Usually Avoided.*** — In every-day chemical work, since our object is usually to prepare some one substance, chemists either avoid chemical changes which are notably reversible, or adjust the conditions, as is done in the foregoing illustrations, so that the reverse of the action which they desire is prevented. In consequence of this, when carrying out the directions for making familiar preparations, the fact that such actions are reversible at all very readily escapes our notice. Arranging the conditions so that the separation of a solid body by precipitation, or the liberation of a gas, takes place, are the two commonest ways of rendering a reversible action complete. Excellent examples of both of these are furnished by the chemical change used in producing hydrogen chloride by the interaction of salt and sulphuric acid, the discussion of which (p. 208) should now be studied attentively in the light of these explanations.

The escape of one member of a system engaged in chemical interaction, because it is gaseous or solid, and in either case immiscible with the rest of the members of the system, is the commonest cause of the obstruction of one direction of a reversible action and the triumph of the other. This, as we have seen, is the combined result of the natural behavior of a system in chemical equilibrium, and of the physical properties, particularly the solubility, of the members of the system. Two rules, attributed to Berthollet, have been made, however, to describe these special cases of a broader principle. Unfortunately, it is difficult so to word them that they shall be entirely unambiguous and entirely correct.

The "rule of precipitation," for example, might read: When certain classes of materials are brought together in solution, if an exchange of radicals would produce an insoluble body, this exchange will occur. But then the fact is that, in such cases, the exchange always occurs to some extent whether any product is insoluble or not. The insolubility is responsible only for the greater completeness of the exchange. Crude statements to the effect that "when an insoluble body can be formed, it will be formed," when close scrutiny shows them to possess any definite meaning whatever, are grossly misleading. They suggest that insolubility is a sort of especially desirable career on which the elements are ambitious of entering.

All forms of these so-called laws are objectionable, because they necessarily suggest that the positive direction of the action is assisted by the immiscibility of the product, and this is the precise converse of the fact. The immiscibility does nothing at all towards assisting the formation of the insoluble substance itself, but does whatever it can towards preventing the destruction of that substance, once it is formed, by hampering the negative action.

**Affinity vs. Solubility.** — The question of the relation of affinity to the apparently much greater efficiency of one of the directions of some reversible actions, may now be put in a much clearer light (pp. 209, 127, and this Chap.). The whole of the possibilities of progress for any action are expressed by a function (p. 295) of the form  $c_1 c_2 k = S$ . If *any one* of the variables, say one of the concentrations ( $c_1$ ), is negligible, the product must be small, irrespective of the values of the other factors. Thus the feebleness of a chemical action only shows that the product of all the variables is minute, and not that the affinity factor *per se* is of small magnitude.

**History.** — The conceptions discussed in this chapter are not new, although they have come into general use rather recently. The law of reaction speed, and the influence of the concentrations of the reacting substance thereon (p. 291), was set forth and formulated by Wilhelmy as early as 1850. Gladstone (1855) studied quantitatively the influence of concentration in cases of chemical equilibrium (p. 292). The kinetic explanation (p. 289) was developed by Williamson (1851). Finally the laws of chemical equilibrium were formulated more explicitly and applied more thoroughly by two Norwegian chemists, Guldberg and Waage (1864–9).

**The Influence of Temperature on the Speed of any Reaction.** — The activity of chemical change, and therefore the speed of all chemical changes, is increased by raising the temperature and diminished by lowering it (*cf.* p. 93). Thus, zinc displaces hydrogen more rapidly from hot than from cold hydrochloric acid. Different actions are affected in different degrees, and no simple rule accurately defining the effect can be given. Roughly speaking, however, a rise of  $10^\circ$  doubles the speed of every action. A rise of  $100^\circ$  will therefore make the speed roughly 1024 times greater. Hence, when the chemist finds that two substances show no evidence of interaction, he infers that there must be either slow action or none, and he seeks to settle the question quickly by heating the mixture.

**The Influence of Temperature on a System in Equilibrium.** — In a reversible change the two opposing reactions are different actions and their speeds are therefore affected in different degrees by the same alteration in temperature. Hence, when the temperature is changed, the relative amount of the two sets of materials present is altered and the equilibrium is displaced. Thus,

in Deacon's process, a rise of  $40^{\circ}$  in the temperature displaces the equilibrium backward (p. 217), and diminishes the yield of chlorine by 5 per cent. In the vapor of phosphorus pentachloride (p. 260), the displacement is in the opposite direction. The vapor is a mixture of the pentachloride with the trichloride and free chlorine:  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ . At  $200^{\circ}$  and 760 mm., 51.5 per cent of the material is present as pentachloride and 48.5 per cent as trichloride and chlorine. Raising the temperature to  $250^{\circ}$  (760 mm.) changes the proportions to 20 per cent and 80 per cent, respectively. At  $300^{\circ}$  only 3 per cent of the pentachloride remains. Evidently, here, raising the temperature favors the decomposition of the pentachloride, and therefore increases the speed of its dissociation more than it does the speed of the reunion of the trichloride and chlorine.

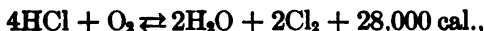
**Van't Hoff's Law.** — One use of a law is to enable us to answer a question, when we have not in memory the fact constituting the answer, and even when we have never read or heard the fact. The law or rule enables a little reasoning to take the place of a vast amount of memorizing. Thus, to answer the question: Does sodium chloride always have the same composition, it is not necessary to have read and to remember all, or any of the numerous investigations of this substance that have been made. We simply refer the question, mentally, to the law of definite proportions, and say "yes." Now the facts mentioned above are connected by a law which will answer many practical questions in chemistry.

When phosphorus trichloride and chlorine combine (to form  $\text{PCl}_5$ ), *heat is given out*. Conversely, when phosphorus pentachloride dissociates, *heat is absorbed*:



Now, when the temperature is *raised*, the action proceeds in the direction of decomposing more of the pentachloride. That is, the equilibrium is displaced in the direction which *absorbs heat*.

In Deacon's process, we find that the interaction of hydrogen chloride and oxygen *liberates heat*,



and in this action *raising* the temperature drives the equilibrium backward, and a *lowering* in the temperature is required to increase the yield of chlorine.

The rule is obvious, and applies to all reversible reactions: **When**



the temperature of a system in equilibrium is raised, the equilibrium point is displaced in the direction which absorbs heat. In other words, a rise in temperature favors the interaction of that one of the two sets of materials to which the heat is added (+ sign) in the equation. If the equation happens to be written with a negative heat of reaction (*e.g.*, p. 100), the heat can, of course, be transferred to the other side with its sign changed. This law is known as *van't Hoff's law of mobile equilibrium*.

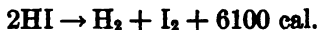
We have already encountered numerous illustrations of this law. The interaction of steam and iron (p. 116) is exothermal, and so the higher the temperature, the more conspicuous the reverse action becomes. Again, as the temperature rises, barium peroxide gives a higher pressure of oxygen (p. 82), hydrates give a greater pressure of water vapor (p. 151), and the dissociation of molecular hydrogen increases (p. 253), because these actions all absorb heat. Many other examples will be noted as we reach them (see ozone, ammonia, nitric oxide).

This law is of practical value. More than once, in chemical factories, much time and money have been spent on trying to arrange machinery to give a better yield of some substance at a high temperature, when a reference to this law would have shown that the chief change necessary was to use a lower temperature, and perhaps hasten the action by use of a contact agent.

*Application to Hydrogen Iodide.*—At 283°, a mixture of hydrogen and iodine yields 82 per cent of hydrogen iodide and 18 per cent of the uncombined elements. At 445°, the yield of hydrogen iodide is 79 per cent, and at 508° only 76 per cent. Since the elements increase in quantity as the temperature rises, we infer that the dissociation of the compound absorbs heat. At 400°, the value is:



Curiously enough, at low temperatures, the action is exothermal. Thus at 18°:



A reversal of the sign of the heat of a reaction is not uncommon. Thus, ammonia and hydrogen bromide, up to about 320°, give out heat in combining. Beyond that temperature, ammonium bromide gives out heat in dissociating (A. Smith), and so beyond that temperature the degree of dissociation is *less* the higher the temperature

(with 135 mm. pres. 35 per cent at 330°, and 20 per cent at 390°). Such reversals are common in cases of ionization (*q.v.*).

**Application to Physical Equilibria.** — Van't Hoff's law applies also to physical processes. Thus, as the temperature rises, a substance which absorbs heat in dissolving will become more soluble. This is the commoner case, as is shown by the way in which most solubility curves (Fig. 79, p. 191) ascend with rising temperature. Conversely, a substance which gives out heat when dissolving in a solution already almost saturated with the compound is *less* soluble with rising temperature. For example, anhydrous sodium sulphate gives out heat in dissolving, and so its solubility diminishes (Fig. 80, p. 193) with rising temperature.

Again, the vaporization of a liquid absorbs heat, and so an increase in temperature will increase the pressure, and therefore the concentration of its vapor (p. 146).

**Le Chatelier's Law.** — The above mentioned law is really a particular case of a more general one. **If some stress (*e.g.*, by change of temperature, pressure, or concentration) is brought to bear on a system in equilibrium, the equilibrium is displaced in the direction which tends to undo the effect of the stress.** Thus, raising the temperature furthers the change which absorbs heat — and therefore would tend to lower the temperature. Increasing the concentration of the molecules pushes the action in the direction which uses up these very molecules (p. 291). Again pressure causes ice to melt, because the water which is formed occupies a smaller volume, and this change tends to relieve the pressure. But pressure will not cause most substances to melt, because usually the liquid form occupies a greater volume and its production would tend to increase pressure.

**Summary.** — In this chapter three questions are answered:

1. Why do some chemical actions cease, while still incomplete?

Answer: They are reversible.

2. What explains the position of the equilibrium point? An-

swers: (a) Equal effects of opposed molecular actions; (b) Equality in speed of opposed reactions.

3. What will displace the equilibrium point? Answer: (a)

Change in concentration of one (or more) of the substances; (b)

Change in the temperature.

**Exercises.** — 1. Why is the formation of the following substances complete: (a) silver chloride (p. 20), (b) hydrogen chloride, and (c) water by union of the elements?

2. How could the interaction of chlorine and water (p. 223) be brought to completion?

3. Explain why the decomposition of potassium chlorate is complete.

4. In view of the statement on p. 80, explain why mercuric oxide is completely decomposed by heating. Point out the resemblance between this experiment and the imaginary one illustrated in Fig. 97 (p. 302).

5. Why can magnetic oxide of iron be reduced completely by a stream of hydrogen (p. 127), and iron oxidized completely by a current of steam (p. 116)?

6. With the phosphorus pentachloride system, say at  $250^{\circ}$ , what effect would suddenly enlarging the space containing a given amount of the vapor produce? What would be the effect of diminishing the space? What would be the effect of introducing additional chlorine into the same space (p. 299)?

7. By what practical means could the degree of dissociation of sulphur vapor ( $S_8$ ) be reduced, without changing the temperature (p. 261)?

8. What inference should you draw from the fact that: (a) the solubilities of potassium nitrate, sodium chloride, and Glauber's salt (p. 191) increase with rise in temperature (p. 305); (b) that those of calcium hydroxide (p. 190) and triethylamine decrease with rise in temperature?

9. Is the heat of solution of lead nitrate (p. 191) positive or negative?

10. Carry out the calculation of  $S$  for 4 and 8 hours (p. 297).

11. What is the molecular concentration of the oxygen in the air (pp. 9, 294), of the nitrogen in the air, of the aqueous vapor above water at  $10^{\circ}$  and at  $20^{\circ}$  (p. 146), of a solution containing one formula-weight of sodium chloride in 10 liters, of a solution containing 65 g. of hydrogen iodide in 250 c.c.?

12. What are the partial pressures of the three components of phosphorus pentachloride vapor at  $250^{\circ}$  and 760 mm. (p. 260)? What are their molecular concentrations?

13. Using the model on p. 298, study the dissociation of  $KI$ , (p. 276), of iodine vapor (p. 276), and of hydrogen iodide (p. 306), and the formation of ferric thiocyanate (p. 292). Show in each case

the effect on the system of increase in volume without change in the amount of material (p. 299).

14. What actions in Chap. XIV are complete for the same reason that the action of sulphuric acid on salt (pp. 207-209) is so?

15. At a given temperature, would increasing the pressure in a mixture of hydrogen and bromine vapor render the union more or less complete? Is the action more complete at a high or at a low temperature?

16. How could a hydrate be completely dehydrated?

#### SUMMARY OF PRINCIPLES

The summary of some of the chief principles of the science (p. 229) may now receive several important additions. For the sake of completeness, reference to the periodic system is made in No. 21, to isomers in No. 22, and to the phase rule in No. 23, although these subjects have not yet been taken up.

15. That weight of each *substance* which in the gaseous condition occupied the same volume as 32 grams of oxygen, temperature and pressure being alike for both (namely, 22.4 liters at 0° and 760 mm.), is taken as the chemical unit of weight for the substance, and is known as its *molar weight* (p. 236).

16. That weight of each *element* which is the greatest common measure of the quantities of the element found in the molar weights of its compounds is taken as the chemical unit of weight for the element, and is known as its *atomic weight*. This weight has the property described in 6 (p. 230).

The composition of each substance is expressed in terms of the atomic weights as units, and the sum of the atomic weights is multiplied by an integer, when necessary, so as to equal the molar weight (p. 249).

17. The number of equivalent weights of hydrogen which combine with, or are replaced by the atomic weight of an element is called the valence of the element (p. 132).

18. The speed of every interaction is a function of the first, or some higher power of the molar concentration of each interacting substance (p. 294).

19. Substances undergoing, at a fixed temperature, an interaction which is reversible, reach a condition of equilibrium. The final proportions of the materials are such that the speeds (see 18) of the opposed actions are equal (p. 290).

20. Van't Hoff's law and Le Chatelier's law (pp. 305, 307).

21. Each *element* has its own set of chemical relations (pp. 226, 284): *e.g.*, it can exist in combination with certain other elements; it has a certain valence, and may have more than one valence; it confers certain properties on its compounds as a class; it is metallic or non-metallic (pp. 150, 284); it resembles certain other elements in several of these respects (*e.g.*, the halogens), and differs from others, in a way more or less definitely described by its place in the periodic system (*q.v.*).

In complex cases, the inter-relations of the elementary units in a compound,

and the relations of the compound to other compounds (see No. 22), are represented graphically by formulæ based upon an hypothesis of molecular structure (pp. 263, 322).

22. Identical combinations of matter may constitute more than one compound substance (isomers, see Urea). These may have equal molar weights (optical and structural isomers), or they may have different molar weights (polymers, pp. 250, 282).

23. In a system in equilibrium the number of components plus two equals the number of phases plus the number of degrees of freedom (Phase rule, *q.v.*).

## CHAPTER XVI

### OZONE AND HYDROGEN PEROXIDE

A FRESH, penetrating odor, resembling that of very dilute chlorine, was noticed by van Marum (1785) near an electrical machine in operation. Schönbein (1840) showed that the odor was that of a distinct substance, which he named ozone (Gk. *ὄζειν*, to smell), and he discovered a number of ways of obtaining it. It is questionable whether there is any ozone in the air, excepting temporarily in the immediate neighborhood of a natural or artificial discharge of electricity.

*Formation of Ozone.* — The most significant way in which ozone is formed is by heating oxygen. The proportion, at equilibrium, increases as the temperature rises. This shows that it is formed with absorption of heat (van't Hoff's law, p. 305).



The percentages of ozone formed are: at 1296°, 0.1 per cent; at 2048°, 1.52 per cent; at 4500°, 16.5 per cent. If the mixture is allowed to cool slowly, the proportion diminishes as the temperature falls, by reversal of the above reaction until, at 300° or below, the amount is practically zero. Rapid cooling, however, to room temperature, at which this reaction is very slow, will preserve most of it. A convenient way of demonstrating its formation by heating is to immerse a platinum wire, heated white hot by an electric current, or a small jet of burning hydrogen, under the surface of some liquid air. The ozone is formed close to the hot wire or flame, and is instantly cooled as it leaves that region by contact with the liquid air (−190°), and so 1.5–2 per cent of it is found in the gases evaporated by the heat. A recognizable trace of ozone is even formed when a small jet of oxygen is blown through the tip of a Bunsen flame.

Ozone is found in the oxygen generated by electrolysis of dilute sulphuric acid (p. 120). It arises during the slow oxidation of phosphorus by the air, resulting, probably, from the decomposition of

unstable, highly oxidized bodies which are formed during the action. Oxygen containing as much as 15 per cent of it is produced by the interaction of fluorine and water (p. 281).

**Preparation of Ozone.** — The most satisfactory way of preparing ozone  $O_3$  is to furnish the necessary energy by allowing electric waves to pass through oxygen. The apparatus (Fig. 98) consists of two co-axial glass tubes, between which the oxygen flows. The

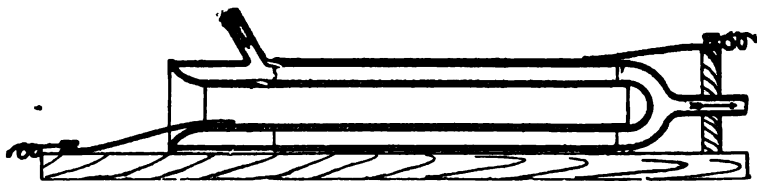


FIG. 98.

waves are generated by connecting an outer layer of tinfoil on the outer tube, and an inner layer of tinfoil in the inner tube with the poles of an induction coil. With dry, cold oxygen, about 7.5 per cent of the gas is turned into ozone. Etching the surface of the glass next to the oxygen with hydrogen fluoride improves the yield.

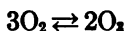
**Physical Properties of Ozone.** — Ozone is a gas of blue color. It boils at  $-119^\circ$ , so that when a mixture of oxygen and ozone is led through a U-tube immersed in liquid oxygen ( $-182.5^\circ$ ), the ozone is liquefied. The deep-blue fluid contains only about 14 per cent of oxygen, and this may be removed by evaporation. When this liquid is distilled, the last portion contains **oxozone**  $O_4$  (C. Harries), which constitutes about 11 per cent of the ozone made by the use of electric waves.

Ozone is much more soluble in water than is oxygen. At  $12^\circ$ , 100 volumes of water would dissolve 50 volumes of the gas at one atmosphere pressure. Its solubility, when mixed with oxygen, is in proportion to its partial pressure (p. 189).

**Chemical Properties of Ozone.** — Ozone can be kept decomposed only when mixed with much oxygen. Hence its density and molar weight cannot be ascertained save by indirect means. The weight of a liter of the mixture at  $0^\circ$  and 760 mm. having been measured, the ozone may be removed by absorption in turpentine and the volume of it present in the gaseous mixture be thus ascer-

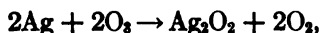
tained. For example, if the weight of 1 l. was 1.468 g. and 50 c.c. were absorbed by turpentine, there were 950 c.c. of oxygen. The weight of this oxygen is  $1000 : 950 :: 1.429 : x$ , from which  $x = 1.361$  g. The rest of the weight,  $1.468 - 1.361$  or  $0.107$  g., was that of 50 c.c. of ozone. The weight of 1 l. of ozone at  $0^\circ$  and 760 mm. is therefore 2.140 g. The molecular weight (weight of 22.4 l.) is thus 47.9 g., or nearly 48 g. The formula of ozone is therefore  $O_3$ .

When produced in cold oxygen, by energy from electric waves, it decomposes slowly. But this change, like all others, is hastened by raising the temperature. Equilibrium, with almost no ozone, is reached instantly at  $250-300^\circ$ . Liquid ozone sometimes decomposes explosively. As the equation shows:

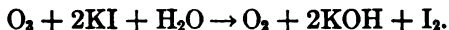


three volumes of oxygen give two volumes of ozone. That this equation, showing that three molecules of oxygen give two molecules of ozone, is correct, may be demonstrated by measuring the diminution in volume which accompanies the action. If a shrinkage of 5 c.c. is observed in forming the ozone, it is found that 10 c.c. more are then absorbed by turpentine. Thus the ozone occupied 10 c.c., and the total oxygen from which it was made was therefore 15 c.c. Hence three volumes of oxygen give two of ozone.

Ozone is a much more active **oxidising agent** than is oxygen. Mercury and silver, which are not affected by the latter, are converted into oxides by the former. Silver gives the peroxide,  $Ag_2O_2$ :



and this action is used as a test for ozone. Paper dipped in starch emulsion containing a little potassium iodide is also used as a test:



The iodine gives a deep-blue color to the starch (*cf.* p. 276). This test, however, will not distinguish ozone from chlorine or hydrogen peroxide, and may, therefore, be used only in the absence of these substances. The last substance is always present in the air and, since air usually shows the above action, is probably responsible for the belief that air contains ozone. The action on silver has never been obtained with air.

Ozone also removes the color from many of the vegetable coloring matters and artificial dyes. It should be understood that the great majority of the complex compounds of carbon are colorless.



acid. The second is largely employed in the commercial manufacture of hydrogen peroxide. In each case, great care has to be taken to precipitate the other products and all impurities from the solution. When hydrochloric acid is used, for example, the barium chloride produced by the action is removed by adding silver sulphate:



An aqueous solution is also obtained by passing carbon dioxide through barium peroxide suspended in water:



Pure hydrogen peroxide is isolated from any of these solutions by distillation under reduced pressure. To secure the low pressure, the ordinary distilling apparatus (Fig. 20, p. 43) is made completely air-tight, and is connected by a branch tube with a water-pump. Hydrogen peroxide is much less volatile than water, but decomposes into water and oxygen violently at 100°. Hence the lower pressure is required to make possible its volatilization at a temperature below this point. At 26 mm. pressure, the water begins to pass off first (at about 27°). The last portion of the liquid boils at 69° and is almost all hydrogen peroxide.

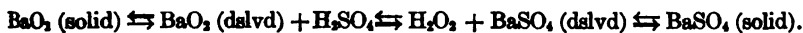
By evaporating the commercial (3 per cent) solution at 70°, a liquid containing 45 per cent of hydrogen peroxide may be made without much loss of the material by volatilization.

Hydrogen peroxide was formerly separated from the other substances produced in the reaction for its preparation, and from a large part of the water, by repeatedly shaking the mixture with ether (*cf.* p. 180). The relative solubility in water and ether is 1 : 0.0596, however, so that much ether is needed. The ethereal layer, which rises to the top, when evaporated, leaves a strong aqueous solution of the compound behind. Explosive substances are often formed by interaction with the ether (perhaps ethyl peroxide  $(\text{C}_2\text{H}_5)_2\text{O}_2$ ), however, and so this method is no longer employed.

#### *The Interaction of Barium Peroxide and Sulphuric Acid.*

— It is worth noting that, although common barium peroxide is not less soluble in water than is the hydrated form used above, it dissolves much more slowly. The fact that it is made by heating barium oxide in oxygen and is composed of compact particles is perhaps accountable for this.

Every action upon a little-soluble, or slowly dissolving body, like the barium peroxide in the above actions, is rather complex. It is only the dissolved part of the substance that interacts. There is thus a physical equilibrium between the undissolved and the dissolved bodies,  $\text{BaO}_2 \text{ (solid)} \rightleftharpoons \text{BaO}_2 \text{ (dissd)}$ , the displacement of which furnishes the material for the chemical action. The latter has therefore to follow the pace set by the former. When barium sulphate is precipitated, another physical equilibrium follows the chemical change:  $\text{BaSO}_4 \text{ (dissd)} \rightleftharpoons \text{BaSO}_4 \text{ (solid)}$ . When relatively insoluble bodies are used or produced, there is thus a chain of equilibria each depending on the others:

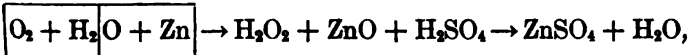


If the barium sulphate ceased to be precipitated, its interaction in solution with the hydrogen peroxide would drive the central action backwards, and barium peroxide would be precipitated instead. The success of the process thus depends on the fact that barium sulphate is less soluble than is barium peroxide.

When carbon dioxide is used (see above), a similar chain of equilibria exists, and in that case it is the barium carbonate that is the less soluble substance.

**Other Modes of Formation.** — Hydrogen peroxide is found in minute amounts in rain and snow. It is formed by the direct union of hydrogen and oxygen. When a hydrogen flame is allowed to play upon ice, appreciable amounts of the peroxide are saved from being decomposed, as they ordinarily would be by the heat of the action, and are found in the water. It is formed also to the extent of 37 per cent when electric waves pass through a mixture of hydrogen and oxygen cooled by liquid air ( $-190^\circ$ ). It is produced when oxygen is passed, close to the negative electrode, through the liquid in an electrolytic cell containing dilute sulphuric acid. The gas is reduced by the hydrogen being liberated on the platinum plate.

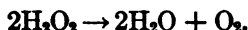
Traces of hydrogen peroxide are formed when zinc, copper, lead, and other metals are shaken with air and very dilute sulphuric acid (1 : 55 Aq). It has been suggested that the water loses its oxygen to the zinc and gives its hydrogen to the oxygen:



the action being assisted by the tendency of the zinc oxide to act with the sulphuric acid to give zinc sulphate.

**Physical Properties.**—Hydrogen peroxide is a syrupy liquid (density 1.46). It blisters the skin, and, when diluted, has a disagreeable metallic taste. It has been frozen (m.-p.  $-0.8^{\circ}$ ), and boils at 26 mm. pressure at  $69^{\circ}$  and at 46 mm. at  $80^{\circ}$ .

**Chemical Properties.**—Hydrogen peroxide (100 per cent) is very **unstable**, and decomposes slowly even at  $-20^{\circ}$ . The dilute aqueous solution, when free from impurities, keeps fairly well. The presence of a trace of free acid increases its stability. Free alkalis and most salts assist the decomposition; hence the necessity for purifying the commercial solution. Since free acids must not be used to stabilize solutions for medical use, a trace of some organic compound which has the same effect (several such are known) is added. Addition of powdered metals, of manganese dioxide, and of charcoal causes effervescence even in dilute solutions, and oxygen escapes:



The 3 per cent, commercial solution yields in this way ten times its own volume of oxygen, and so is often labelled "10 vol. solution." The more concentrated solutions (38 per cent) remain quiescent in a dish of polished platinum even at  $60^{\circ}$ , but the making of a slight scratch on the bottom, beneath the surface of the liquid, causes profuse liberation of oxygen along the sharp edge thus produced. The action of these contact agents is therefore probably mechanical.

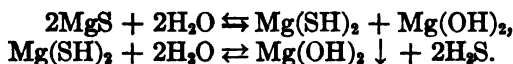
Since the substance cannot be vaporized, even at low pressure, without some decomposition, its **molar weight** has been determined by the freezing-point method (p. 199). The freezing-point of a 3.3 per cent solution in water is  $2.03^{\circ}$  below that of the water itself. Hence, in 1000 g. of water, 3.3 g. would have given a depression of  $2.03 \times 96.7 \div 1000$ , or  $0.196^{\circ}$ . Therefore a depression of  $1.86^{\circ}$ , the average depression produced by one mole of a substance in 1000 c.c. of water (see p. 335), would have been caused by  $3.3 \times 1.86 \div 0.196$ , or 31.3 g., which is the required molar weight. Now the formula HO corresponds to a molar weight of 17 and  $\text{H}_2\text{O}_2$  to one of 34. It is evident, therefore, that the latter is the correct formula.

Hydrogen peroxide, in solution in water, is a **feeble acid**. The normal molar weight and very small electrical conductivity (see Chap. XVIII) show that only a very small proportion of it can be ionized. As an acid it enters into double decomposition readily and the peroxides are salts with the negative radical  $\text{O}_2^{\text{II}}$  (**peroxides**).

is used in medicine and as a cosmetic. The carbonates are not precipitated in the presence of ammonium salts, and interact with such salts in the same way as does the hydroxide.

**Magnesium Sulphate  $MgSO_4$ .**— The common **heptahydrate**  $MgSO_4 \cdot 7H_2O$  crystallizes from cold water in rhombic prisms, and is called **Epsom salts**. At  $0^\circ$  a **dodecahydrate** appears. The heptahydrate is efflorescent, and loses its water by stages and with decreasing aqueous tension. The **monohydrate**, found in the salt layers as **kieserite**  $MgSO_4 \cdot H_2O$ , has a very low aqueous tension, and is not rapidly dehydrated except above  $200^\circ$ . The hepta- and monohydrates present a striking case of difference in solubility in two forms of one salt, the former giving at  $15^\circ$  a solution containing 33.8 g. of the sulphate in 100 g. of water, while the latter is almost insoluble. Magnesium sulphate is used in the manufacture of sodium and potassium sulphates, and is employed also for "loading" cotton goods, and as a purgative.

**Magnesium Sulphide  $MgS$ .**— The sulphide may be formed by heating the metal with sulphur. It is insoluble in water, but is decomposed and gives, finally, hydrogen sulphide and magnesium hydroxide:



The hydrolysis is more complete than in the case of calcium sulphide, and eliminates all the hydrogen sulphide, because magnesium hydroxide is much more insoluble than is calcium hydroxide, and so there is little reverse interaction tending to reproduce the soluble hydro-sulphide  $Mg(SH)_2$ .

**Phosphates of Magnesium.**— The only phosphate of importance is **ammonium-magnesium orthophosphate**  $NH_4MgPO_4 \cdot 6H_2O$ , which appears as a crystalline precipitate when sodium phosphate and ammonium hydroxide (and chloride, p. 766) are mixed with a solution of a magnesium salt. This compound is insoluble in water containing ammonium hydroxide, and is used in quantitative analysis for estimating both magnesium and phosphoric acid. Before being weighed the precipitate is ignited, and is thus converted into the anhydrous pyrophosphate of magnesium  $Mg_2P_2O_7$ . The salt  $NH_4MgAsO_4 \cdot 6H_2O$  has similar properties, and is used for estimating arsenic acid.

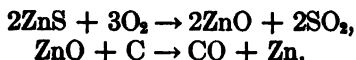
**Analytical Reactions of Magnesium Compounds.**—The magnesium ion  $Mg^{++}$  is colorless and bivalent. It does not enter into complex ions. Soluble carbonates precipitate basic carbonates of magnesium, but not when ammonium salts are present. The latter limitation distinguishes compounds of magnesium from those of the calcium family. Potassium hydroxide precipitates the hydroxide of magnesium, except when salts of ammonium are present. The mixed phosphate of ammonium and magnesium, in presence of ammonium hydroxide, is the least soluble salt.

### ZINC ZN

**Chemical Relations of the Element.**—Zinc is bivalent in all its compounds. Of these there are two sets, — the more numerous and important one in which zinc is the positive radical ( $Zn.SO_4$ ,  $Zn.Cl_2$ , etc.), and a less numerous set, the zincates, in which zinc is in the negative radical ( $Na.HZnO_2$ , etc.). Both sets of salts are hydrolyzed by water, as the hydroxide is feeble whether it is considered as an acid or as a base. The element also enters into complex cations and anions. The salts are all poisonous.

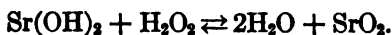
**Occurrence and Extraction from the Ores.**—The chief sources of zinc are calamine  $Zn_2SiO_4.H_2O$ , smithsonite  $ZnCO_3$ , zinc blende (Ger. *blenden*, to dazzle) or sphalerite  $ZnS$ , franklinite  $Zn.(FeO_2)_2$ , and zincite  $ZnO$ . The red color of the last is due to the presence of manganese.

The ores are first concentrated by froth flotation (p. 737). They are then converted into oxide — the carbonate by ignition, and the sulphide by roasting. The sulphur dioxide is used to make sulphuric acid. A mixture of the oxide with coal is then distilled in earthenware retorts at  $1300-1400^\circ$ , the zinc condensing in earthenware receivers, while carbon monoxide burns at a small opening:



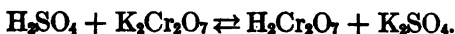
At first zinc dust, a mixture of zinc and zinc oxide, collects in the receiver, and afterwards liquid zinc. The product, which is cast in blocks, is called spelter. It contains small amounts of lead, arsenic, iron, gallium, and cadmium, because the sulphides of these metals are almost invariably present in zinc-blende. The amounts of spelter manufactured (1913) were United States 346,700 short tons, Germany 312,000, Belgium 218,000, Great Britain 65,000.

thus, when it is added to solutions of barium and strontium hydroxides, the hydrated peroxides appear as crystalline precipitates:



The precipitation involves another equilibrium:  $\text{SrO}_2 + 8\text{H}_2\text{O} \rightleftharpoons \text{SrO}_2 \cdot 8\text{H}_2\text{O}$  (solid).

The formation of a beautiful blue substance by the action of hydrogen peroxide upon dichromic acid is used as a test. The test is carried out by adding a drop of potassium dichromate to an *acidulated* solution of the peroxide. The acid interacts with the dichromate, giving free dichromic acid:

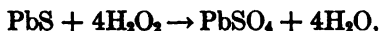


The blue substance, which is very unstable and quickly decomposes, is a perchromic acid. A blue, crystalline perchromic acid  $(\text{HO})_4\text{Cr}(\text{OOH})_2$ , which decomposes above  $-30^\circ$ , has been prepared. The blue substance has the property, unusual in inorganic compounds, of dissolving much more readily in ether than in water. It is also much less unstable when removed from the foreign materials in the aqueous solution. Hence the test is rendered more delicate by extracting the solution with a small amount of ether. In the ethereal layer the color of the compound is more permanent, as well as more distinctly visible on account of the greater concentration.

Hydrogen peroxide is a much more active oxidizing agent than free oxygen. This would be expected from the fact that it contains so much more energy than the water and oxygen into which it decomposes (p. 318):  $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O} + 23,100 \text{ cal.}$  Thus, it liberates iodine from hydrogen iodide, an action which, in presence of starch emulsion (*cf.* p. 276), is used as a test for its presence:



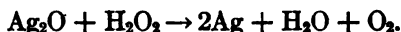
It converts sulphides into sulphates. The white lead (*q.v.*) used in paintings is changed by the hydrogen sulphide in the air of cities to black lead sulphide,  $\text{Pb}_2(\text{OH})_2(\text{CO}_3)_2 + 3\text{H}_2\text{S} \rightarrow 3\text{PbS} + 4\text{H}_2\text{O} + 2\text{CO}_2$ . This may be oxidized to white lead sulphate by means of hydrogen peroxide:



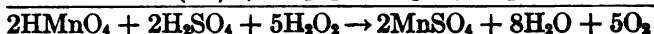
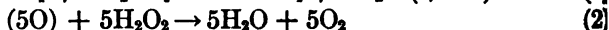
and in this way the original tints of the picture may be practically restored. Organic coloring matters are changed into colorless substances by an action similar to that of ozone (*cf.* p. 314). Hence

hydrogen peroxide is used for bleaching silk, feathers, hair, and ivory, which would be destroyed by a more violent agent. The products of its decomposition, being water and oxygen only, are harmless, and, on this account, it is used in disinfecting (destroying organisms in) infected sores, and as a throat wash.

Hydrogen peroxide exercises the functions of a **reducing agent** in special cases, also. Thus, silver oxide is reduced by it to silver:



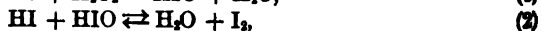
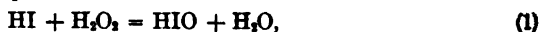
A solution of potassium permanganate, in which the permanganic acid has been set free by an acid,  $\text{KMnO}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{HMnO}_4 + \text{KHSO}_4$ , is rapidly reduced. The permanganic acid, with excess of sulphuric acid, tends to undergo the first of the following changes, *provided a substance is present which can take possession of the oxygen that would remain as a balance*:



In all reductions by hydrogen peroxide, each molecule of the latter removes but one atomic weight of oxygen from the other substance. Whether it behaves thus because its two hydrogen units combine with *this* oxygen and *all its own* oxygen escapes, or because it furnishes water and *one* oxygen unit of the pair required to form the molecule of free oxygen (the substance reduced furnishing the other), has not been determined.

The above action is used in quantitative analysis for estimating the quantity of hydrogen peroxide in a given liquid after the liquid has been acidified. The amount of a standard (p. 277) solution of the permanganate which is required to decompose all the peroxide is measured by means of a burette (*q.v.*). The permanganate is deep reddish-purple in color, while the products are colorless. Hence, after the peroxide is exhausted, the next drop of the permanganate confers a distinct, permanent, pink tinge upon the liquid. The addition of the permanganate solution is stopped so soon as this condition is reached and the volume of it that has been used is read off.

The action of hydrogen peroxide on hydrogen iodide proceeds slowly, so that its speed can be measured. Although the equation shows *three* interacting molecules ( $2\text{HI} + \text{H}_2\text{O}_2$ ), a constant (p. 295) is obtained only by using the formula for a reaction involving two molecules (reaction of the second order). This is because the reaction takes place as two consecutive actions:

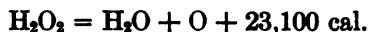


of which (1), in which hypo-iodous acid is formed, alone takes much time. The second (2) is the reverse of the action of iodine on water (cf. p. 277), and is very speedy. Hence the speed measurement concerns only (1), which is dimolecular.

**Thermochemistry of Hydrogen Peroxide.**—The formation of hydrogen peroxide from the free elements is accompanied by evolution of heat:



Hence the substance is formed by direct union (p. 317). But its decomposition into water and oxygen gives out a further supply of heat:



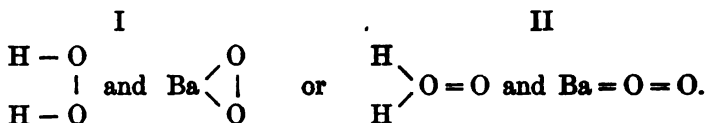
The sum of these two stages, of course, yields the same result (cf. p. 100) as the direct formation of water (68,400 cal.).

When hydrogen peroxide is used, instead of free oxygen, for oxidizing purposes, each such action liberates 23,100 calories of heat more in the former case than it would in the latter. Hence the activity of the substance as an oxidizer (cf. pp. 314, 319).

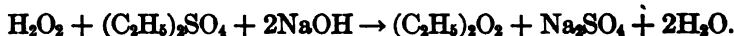
**Chemical Constitution of Peroxides.**—We have seen (p. 317) that when acids act upon barium peroxide  $\text{BaO}_2$ , hydrogen peroxide is formed:  $\text{BaO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$ . But all oxides containing two atoms of oxygen in each molecule do not yield hydrogen peroxide. Thus, lead dioxide  $\text{PbO}_2$  and manganese dioxide  $\text{MnO}_2$ , when treated with sulphuric acid, give the sulphate of the metal and water and oxygen:  $2\text{MnO}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{MnSO}_4 + 2\text{H}_2\text{O} + \text{O}_2$ . We infer from this that the two sets of dioxides are not alike. With barium peroxide there is a simple double decomposition, or exchange of radicals, and so we hold that it contains the radical  $\text{O}_2$  which is bivalent as a whole:  $\text{Ba}^{\text{II}}(\text{O}_2)^{\text{II}}$ . This harmonises with the fact that no other compound is known in which barium has even the appearance of being quadrivalent. Manganese dioxide can give a tetrachloride (p. 219), however, as can also lead dioxide (q.s.), so we infer that the manganese and lead are here quadrivalent, and that the radical is  $\text{O}$ :  $\text{Mn}^{\text{IV}}(\text{O})_2^{\text{II}}$  and  $\text{Pb}^{\text{IV}}(\text{O})_2^{\text{II}}$ . For this reason, we have recently begun to call barium peroxide a salt, and to name it barium peroxidate. Similarly, we have strontium peroxidate  $\text{Sr}^{\text{II}}(\text{O}_2)^{\text{II}}$  and sodium peroxidate  $\text{Na}_2(\text{O}_2)^{\text{II}}$ .  $\text{H}_2(\text{O}_2)^{\text{II}}$  should therefore be called peroxidic acid.



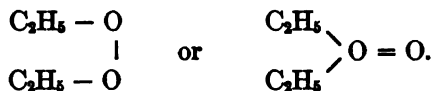
There still remains the question whether hydrogen peroxide and barium peroxide are: .



In other words, whether the negative radical of the peroxides is  $-\text{O}-\text{O}-$  or  $=\text{O}=\text{O}$ . Some compounds in which oxygen is quadrivalent are known, so that the second alternative is worthy of consideration. Now, we have seen that hydrogen peroxide is formed by the reduction of dissolved oxygen (p. 317). On the whole, this favors the symmetrical formula I, rather than the unsymmetrical formula II. Then, hydrogen peroxide is never formed by the oxidation of water. This favors I very distinctly, because it would be more difficult to insert the oxygen to give I than to attach it to the oxygen of the water as in II. Finally, when some ethyl sulphate  $(\text{C}_2\text{H}_5)_2\text{SO}_4$  is dissolved in 15 per cent hydrogen peroxide, and sodium hydroxide is added a drop at a time while the mixture is shaken, the following reaction occurs:



By distillation, the substance  $(\text{C}_2\text{H}_5)_2\text{O}_2$  is obtained (b.-p.  $65^\circ$  at 760 mm.). When zinc dust and acetic acid are added to this product, hydrogen is liberated:  $\text{Zn} + 2\text{HCO}_2\text{CH}_3 \rightarrow \text{Zn}(\text{CO}_2\text{CH}_3)_2 + \text{H}_2$  and the hydrogen reduces the  $(\text{C}_2\text{H}_5)_2\text{O}_2$ , giving alcohol  $\text{C}_2\text{H}_5\text{OH}$  (Baeyer and Villiger, 1900). Now, the compound was either:



The second, on reduction, would be expected to give ether  $\text{C}_2\text{H}_5 - \text{O} - \text{C}_2\text{H}_5$ , which is not formed, while the former would give  $2\text{C}_2\text{H}_5\text{OH}$ , which is formed. Hence formula I is assigned to the peroxides.

Such a formula is called a **structural** or **graphic formula**, because, by means of a construction or graph, it indicates the chemical reactions of the substance. It *may* also indicate the way in which the parts of the molecule are actually connected, but its primary purpose is to indicate chemical behavior. Of course, the number of lines emanating from each symbol must correspond with the valence of the atom concerned.

**Exercises.** — 1. What volume of ozone will be taken up by 100 c.c. of water at  $12^{\circ}$  from a stream of oxygen at 760 mm. containing 7.5 per cent of ozone (p. 312)?

2. Formulate the action of carbon dioxide on barium dioxide (p. 316) after the manner of that of sulphuric acid on the same substance (p. 317). The dissolving gas gives an additional equilibrium:  $\text{CO}_2 (\text{gas}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 (\text{dissd})$ .

3. At what temperature will a ten per cent solution of hydrogen peroxide freeze (p. 318)?

4. Write the thermochemical equations for oxidation of indigo by hydrogen peroxide (pp. 315, 319).

5. How many times its own volume of oxygen gas will a 4 per cent solution of hydrogen peroxide give off when treated with: (a) platinum powder (p. 318); (b) sulphuric acid and potassium permanganate?

6. What per cent of hydrogen peroxide does a "12 vol." solution contain?

## CHAPTER XVII

### DISSOCIATION IN SOLUTION

THE employment of interacting substances in the form of solutions is so constant in chemistry, and the reasons for this are so cogent, that we must now resume the discussion of this subject (cf. p. 178).

The present chapter will be devoted to giving the proofs that the molecules of **acids, bases, and salts**, in aqueous solutions, are **actually dissociated into parts** by the solvent. This will be shown by consideration, successively, of certain peculiarities in the **chemical behavior**, the **osmotic pressures**, the **freezing-points**, and the **boiling-points** of the solutions of these substances. We shall see that these parts coincide in composition with the radicals, and are called **ions**.

*Some Characteristic Properties of Acids, Bases, and Salts, Shown in Aqueous Solution.* — **Acids** all contain hydrogen (p. 120). In aqueous solution, if soluble, they are sour in taste, they turn blue litmus red, and their hydrogen is displaced by certain metals (p. 118), and has the properties of a radical. By the last statement is meant that it very readily exchanges places with other radicals in reversible double decompositions (p. 208). Amongst the acids mentioned have been: hydrochloric acid  $\text{HCl}$ , sulphuric acid  $\text{H}_2\text{SO}_4$ , hypochlorous acid  $\text{HClO}$ , acetic acid  $\text{HCO}_2\text{CH}_3$ , and hydrogen peroxide  $\text{H}_2\text{O}_2$ . Many other bodies, like sugar, kerosene, and alcohol, also, contain hydrogen but not one of them shows all of these properties.

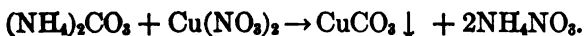
Again, **all salts** (p. 214) are made up of two radicals, and the reversible double decompositions into which they enter with acids, bases, and other salts, consist in exchanges of these radicals. Other substances may include the same combinations of atoms, but in their actions these groupings are often disregarded. Thus, sodium chloride  $\text{NaCl}$  and silver nitrate  $\text{AgNO}_3$  exchange radicals completely (p. 20), and, in dilute solution, hydrogen chloride and sodium hydrogen sulphate do so partially (p. 208). But sodium chloride and nitroglycerine  $\text{C}_2\text{H}_5(\text{NO}_2)_3$  do not interact at all. The latter is not a

salt, although it contains the same proportion of nitrogen to oxygen as does any nitrate.

All bases (p. 149) contain hydroxyl OH as a radical, combined with some positive radical. Potassium hydroxide KOH is soluble and active, zinc hydroxide  $\text{Zn(OH)}_2$  and many others, however, are insoluble. Bases all exchange radicals readily in double decomposition with salts and acids. Other substances, like alcohol  $\text{C}_2\text{H}_5\text{OH}$ , may contain hydroxyl, but do not interact readily with salts like NaCl, and are not bases.

**The Influence of Water and Other Solvents.** — It is chiefly in aqueous solution that these special properties of acids, bases, and salts become apparent. Their behavior is often quite different in the absence of this solvent. If, for example, we mix together dry ammonium carbonate  $(\text{NH}_4)_2\text{CO}_3$  and partially dehydrated, solid cupric nitrate  $\text{Cu(NO}_3)_2$ , and apply heat, a violent interaction begins. An immense cloud of smoke and gas is thrown out of the tube, and the substance remaining is either black or reddish, in parts, according to the proportions of the substances employed. The residue contains black cupric oxide CuO, and sometimes red cuprous oxide  $\text{Cu}_2\text{O}$ . The gas is tinged red by the presence of nitrogen tetroxide  $\text{NO}_2$ , while a more careful examination would show that it contained carbon dioxide, nitrogen, nitrous oxide  $\text{N}_2\text{O}$ , water vapor, and perhaps still other products.

The contrast, when the substances are dissolved in water before being brought in contact with one another, is very great. A pale-green precipitate is formed at once, and rapidly settles out. On examination, this turns out to be a carbonate of copper (basic, see under Copper), while evaporation of the solution furnishes us with ammonium nitrate. There are only two main products, and the essential part of the action in solution may be represented by the equation:



In the interaction between the *dry* substances the molecules are completely disintegrated, the whole change is very complex, and it takes a good deal of time. In the action in water, no heating is required, the substances are neatly broken apart, certain groups of atoms, which we call radicals, are transferred as wholes from one state of combination to another, and the rearrangement takes place instantaneously in a machine-like manner. Contrasts like this be-

tween the interactions of anhydrous and dissolved bodies are very common. Thus, we have had occasion (p. 119) to mention the difference between the action of metals on concentrated and on dilute sulphuric acid.

Many compounds, however, do not show any change in behavior when dissolved in water. Sugar, for example, is, as a rule, more readily acted upon in the absence of any solvent. Then again, while water is not the only solvent which has the effect we have just described, the majority of solvents, if they affect chemical change at all, simply retard it. Thus the union of iodine and phosphorus in the absence of a solvent takes place spontaneously with a violent evolution of heat. When the elements are dissolved in carbon bisulphide before being mixed, the action is much milder, although the product is the same (phosphorus tri-iodide). The diminution in the concentration of the ingredients by solution has simply decreased the speed of the action in the normal way (p. 291). That water and some other solvents (*e.g.*, alcohol) have a specific influence tending to increase the activity of acids, bases, and salts, shows that a special explanation of the phenomenon must be found.

Summing up these points we see that the peculiarity of acids, bases, and salts in *aqueous solution* is that each compound always splits in the same way. Thus, cupric nitrate always gives changes involving Cu and NO<sub>3</sub>, and never interacts so as to use CuN<sub>2</sub> and O<sub>2</sub>, or CuO<sub>2</sub> and NO<sub>2</sub>, as the basis of exchange. Similarly, *dilute* acids always offer hydrogen in exchange, and so nitric acid behaves as if composed of H and NO<sub>3</sub>, and sulphuric acid as if composed of 2H and SO<sub>4</sub>, and never as if made up of HSO and HO<sub>2</sub>, or H<sub>2</sub>S and O<sub>4</sub>. The sour taste and the effect upon litmus seem to be properties of this easily separable hydrogen, for they are shown only by acids. The result is that we can make a list of the units of exchange, such as H, OH, NO<sub>3</sub>, CO<sub>3</sub>, SO<sub>4</sub>, Cu, K, and Cl, employed by acids, bases, and salts in their interactions. The molecule of each compound of these classes contains at least two of them. Even when these units contain more than one atom, their coherence is as noticeable within this class of actions, as is the permanence of the atomic masses themselves in all actions.

The question raised in our minds is whether solution in water alters the character of the molecule simply by producing a sort of *plane of cleavage* in it which creates a predisposition to a uniform kind of chemical change, or whether it *actually divides* the molecules into separate parts consisting of the above units of exchange, and

leaves subsequent chemical actions to occur by cross-combination of these fragments. The fact that the dissolved substances can be recovered by evaporation of the liquid does not demonstrate that they have not been changed temporarily while in solution. The alteration which the water produces, whatever it be, will naturally be reversed when the water is removed. Since our question involves nothing but the counting of particles, the number of which would be much greater in the event that actual subdivision of molecules is the explanation, it can be answered by a study of the physical properties of solutions. Several physical properties may be used, and they give concordant answers to the question. We shall consider the evidence of osmotic pressure, of freezing-points, boiling-points (in this Chapter), and of conductivity for electricity (Chap. XVIII).

### OSMOTIC PRESSURE

In the earlier discussion of solution (p. 184) the condition of a dissolved substance was viewed as akin to that of a gas. We conceived the molecules of the dissolved substance as being distributed through the space occupied by the solvent, as being separate from one another, and as moving about independently of each other. This was because the phenomena of diffusion and osmotic pressure (p. 185) in solution resemble those of diffusion and pressure in gases. The attempt to obtain by calculation, using this theory, the results that are observed, shows that this theory applies, as van't Hoff stated when suggesting it, only to infinitely dilute solutions. It gives a fairly satisfactory explanation of the behavior of extremely dilute solutions, but not of solutions such as are commonly employed in chemical work.

The invention of a suitable hypothesis for the explanation of the facts of osmosis presents some difficulties, but the facts themselves are undoubted. It will conduce, therefore, to clearness if we speak first of some things which may be observed and are true, irrespective of any explanation.

**Phenomena Produced by Osmotic Pressure.** — In order that the osmotic pressure (Gk. *ὀσμός*, impulsion) may be perceived, a partition, which the dissolved molecules are unable to traverse, must be interposed between the solution and a contiguous mass of the pure solvent (Fig. 75, p. 184). The partition must be permeable by the solvent, however. Such a partition is described as **semi-permeable**.

The general nature of the phenomena may be seen by employing a tube (Fig. 99), to which a diffusion shell, of test-tube form, is securely attached. It is charged with sugar solution, and suspended in pure water. This thimble is somewhat permeable by the sugar, but the water traverses it very easily, and so an exhibition of the general result of a stricter test is obtained quickly.

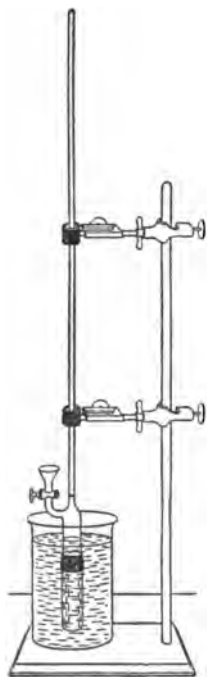


FIG. 99.

The water is able to pass freely through the membrane in either direction, while the sugar is not. As the result of the interchange of water, the liquid rises slowly but steadily in the tube. **The pure solvent always passes into the solution.** If, further, two solutions of different concentrations of the same substance are employed, then, invariably, **water passes from the more dilute solution into the more concentrated one** through the membrane. There is apparently a tendency for the water so to distribute itself that the solutions may eventually become equal in strength. The water passes from a dilute solution, leaving it more concentrated than before, into a more concentrated solution, rendering it more dilute.

These phenomena were first studied by Pfeffer (1877), a botanist, who used certain plant cells for the purpose. The cell content included a liquid containing various salts in solution, and a protoplasmic layer which was not attached to the cell wall. This protoplasmic layer behaved like a semi-permeable membrane. When such cells were immersed in a *concentrated* solution of any substance, *the water passed* from the interior of the cell *to the solution*, and by means of a microscope a shrinkage of the protoplasmic layer away from the cell wall could be observed. Conversely, when such cells were placed in pure water, *or a solution of a very dilute nature*, *water passed* from the outside *into* the interior, and the protoplasmic layer was distended so as to fill the corners completely. The distension of the cells of drooping flowers, when their stems are placed in water, and the consequent revival, is a familiar illustration of the same sort of thing. All solutions which produced neither the one effect nor the other on a given set of plant cells, were named *is-osmotic*. The osmotic pressures of their contents were the same as the pressure of the cell fluid.

Since the entrance of the solvent is due to the dissolved substance, and the solvent is really drawn forcefully into the solution, it might be more appropriate to call the force osmotic suction. Whatever it is named, however, it is real, and its value can be measured.

Professor Crum Brown has devised an arrangement which exhibits the action of a perfectly semi-permeable membrane very strikingly [Lect. exp.]. A concentrated solution of calcium nitrate is shaken with a small amount of phenol (carbolic acid), so as to become saturated with the latter, and the mixture is then poured into a tall, narrow cylinder. The phenol rises and floats upon the surface of the calcium nitrate. The amount of phenol should not be more than sufficient to saturate the liquid and give a layer a few millimeters in thickness. Distilled water, also saturated with phenol, is cautiously introduced above all. The water on both sides of the layer of phenol is soluble in phenol, and consequently, by dissolving in this and passing out on the other side, can traverse the partition. The calcium nitrate, however, which is here the dissolved substance, cannot traverse the phenol in which it is not soluble. The phenol therefore constitutes a perfect semi-permeable membrane. If the level of the lower side of the phenol is marked on the outside of the cylinder by means of a strip of paper, it will be found, as the arrangement is watched from day to day, that the water passes through the phenol into the solution, and the phenol rises higher and higher, until finally it surmounts all the rest of the liquid.

***The Phenomena Logical Consequences of Semi-Permeability.***—The passage of the water into the solution in which the greater osmotic pressure exists seems at first paradoxical. We must remember, however, that the system, consisting of the liquids on each side of the membrane, can be in equilibrium only when the activity of the solvent on the two sides is identical. But the equalization of the activities cannot take place by the passage of part of the solute from one side to the other. The membrane has been taken, purposely, of such a nature that the dissolved substance is unable to traverse it. The equalization must occur, therefore, in the only other possible manner, namely, by the passage of the solvent in the other direction.

An imitation of this behavior may easily be exhibited by the use of gases [Lect. exp.]. A piece of peritoneal membrane is stretched across the mouth of a thistle-tube and moistened with water. The tube, which has been bent in U-form to serve as a manometer, contains a small amount of some colored liquid, whose motions will exhibit any change in pressure in the interior. When an inverted cylinder of ammonia gas is placed round the head of the thistle-tube, the ammonia gas dissolves in the water on the membrane until this water is saturated, that is, until the ammonia molecules leaving the water are as numerous as those entering

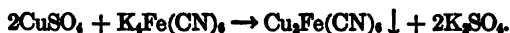


it. It will be seen, however, that the ammonia solution really has two surfaces, one of them towards the interior, and the ammonia molecules must eventually leave both surfaces at the same rate at which they are landing upon one of them. The ammonia gas being at the pressure of the atmosphere, the molecules of ammonia leaving the film will produce a tension of one atmosphere of ammonia over each surface. Thus ammonia gas will be transferred from the cylinder to the interior of the thistle-tube until its partial pressure in the latter is equal to that in the former. The membrane is semi-permeable, since, of the air and ammonia contained in the thistle-tube, only the ammonia can traverse the film. The contents of the thistle-tube therefore correspond to the solution, air being the solute and ammonia the solvent. The original air in the apparatus was at a pressure of one atmosphere, but the ammonia, although under no greater pressure, enters nevertheless. Indeed, it would continue to do so until the pressure inside became equal to that of the ammonia outside plus the original pressure of the air, a total of two atmospheres. The case corresponds to that of water entering a solution whose osmotic pressure is one atmosphere. It enters until the contents of the apparatus are under a pressure one atmosphere greater than that existing outside.

This experiment illustrates the passage of a substance into a region of higher pressure, but must not be held to afford an explanation of how osmotic pressure operates. Osmotic pressure cannot be explained as due to impacts of water molecules alone outside and to impacts of water and solute molecules together inside, the impacts of the latter constituting the excess of pressure inside (see p. 331).

**Measurement of Osmotic Pressure.**— It will be seen that the whole phenomenon rests upon the fact that the membrane used is permeable by one of the components only. The preparation of a vessel of sufficient strength, and possessing walls with the maximum permeability by water and the minimum permeability by dissolved substances, presents great difficulties. A device of Pfeffer's is still found to be the best. A cylinder of porous porcelain, much like a Pasteur filter-tube, is treated so that its pores are partially filled with a gelatinous precipitate of cupric ferrocyanide (*q.v.*).

The porous cylinder, after removal under the air-pump of the air which its walls contain, is placed in a solution of cupric sulphate. Its interior is then filled with a solution of potassium ferrocyanide. When these two liquids meet by diffusion inside the wall, they interact, producing a dense precipitate of the substance above mentioned:



The best membranes are obtained by using a current of electricity to cause the copper to move towards the cell on one side and the ferrocyanide radicals to move towards it from the other side.

If such a prepared vessel, after being filled with a one per cent sugar solution, could be closed by a piston (e.g., Fig. 54) and be placed in pure water, it would be found necessary to place weights on the piston to prevent an upward movement, due to access of water to the interior through the walls. Finally a weight would be found that would just balance the inward tendency of the water. With more weight than this, water would be squeezed out through the pores; with less, the water would force its way in and the piston would rise. When this weight has been placed in position, the water inside and outside, having reached a condition of equilibrium, must be exerting equal pressures on each side of the wall of the vessel. Hence, the excess of pressure inside must be due to the osmotic pressure of the solution. The weight balancing the osmotic pressure at  $15^{\circ}$ , in the case of a one per cent sugar solution, is found to be about 0.76 kg. for every sq. cm. of the exposed surface. Since 1.03 kg. per sq. cm. equals 760 mm., this would indicate a pressure of  $760 \times 0.76 \div 1.03$ , or 572 mm. (0.75 atmospheres).

In practice a small bent tube opening into the cylinder is used as a manometer (Fig. 100). The other end of the tube is closed, and some nitrogen is confined in this end by mercury. The diminution in the volume of the nitrogen registers the pressure. The smaller tube, drawn out to a point, is used for filling the cell with the solution and is then sealed before the blow-pipe. The whole apparatus is immersed in a large bath of water whose temperature can be maintained constant during the experiment. Concordant readings are hard to get in consequence of difficulties inherent in the preparation and use of the apparatus.

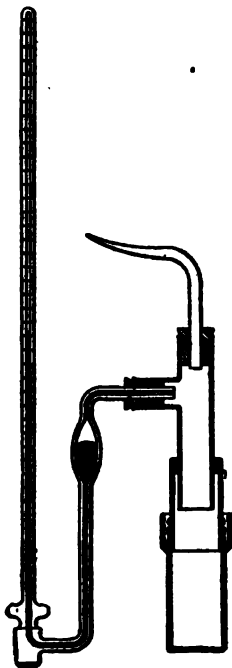


FIG. 100.

**The Exact Relations of Osmotic Pressure.**—The value of the observed osmotic pressure increases with the concentration of the solution. The chief relation is that the osmotic pressure is proportional to the logarithm of the fraction of all the molecules in the

solution which are molecules of the solvent.\* This holds strictly, however, only when there is no chemical interaction between solvent and solute, when there is no change in volume consequent upon solution, and when no heat change occurs upon dilution of the solution. In actual fact many substances form hydrates when dissolved in water. Thus sugar seems to form a penta- or a hexahydrate, and this removes a part of the solvent. Again, changes in volume upon solution are often considerable (p. 201). Also there is always some heat of solution and often (cf. p. 203) the value is very great. Finally, it is impossible in the case of associated liquids like water (cf. p. 202) to tell how many molecules of the solvent, relatively to the number of molecules of the solute, are present, because we do not yet know how many are  $\text{H}_2\text{O}$ , and how many  $(\text{H}_2\text{O})_2$  and  $(\text{H}_2\text{O})_3$ . Furthermore, addition of a solute displaces the equilibrium and alters the proportions of these numbers. It is thus impossible accurately to predict the osmotic pressure of a given solution, or even accurately to calculate the osmotic pressure at one concentration from an observation made at another concentration. That van't Hoff's gas analogy applies to infinitely dilute solutions, but is wholly inapplicable to ordinary solutions, is easily shown. At  $0^\circ$ , a 0.53 molar solution of cane sugar gives an observed osmotic pressure of 13.95 atmospheres while calculation from van't Hoff's theory yields 11.79 atmos., and a 2.2 molar solution gives by observation 133.74 atmos. and by calculation only 49.15 atmos.

Modes of calculation which, so far as possible, take into account the modifying factors mentioned above, cannot be discussed here. It is sufficient to say that **dissolving any substance in water, or some other solvent, reduces the physical activity of the solvent.** Thus pure water is more active than water in a solution, and forces its way through a suitable membrane into the solution. Pure water also shows a higher vapor pressure, and therefore a lower boiling-point (see p. 337).

***Approximate Relations of Osmotic Pressure.***—As an aid to memory, and as a very rough indication of the facts, the following statements, which are approximately true for very dilute solutions, may be made.

The osmotic pressure is proportional to the concentration (parallel of Boyle's law). Thus the values for sugar ( $15^\circ$ ) are: 0.1 molar 2.54 atmos., 0.2 molar 4.99 atmos., 0.4 molar 9.95 atmos.

\* For small concentrations the osmotic pressure may be taken without serious error as proportional to the molar fraction of the solute.

The osmotic pressure increases in proportion to the absolute temperature (parallel of Charles' law). Thus a 0.1 molar solution of sugar gives at 5° 2.45 atmospheres pressure, and at 50° 2.64. A gas which at 278° Abs. gave 2.45 atmos. pressure, would give 2.84 atmos. at 323° Abs., so that the rule is here over 7 per cent in error.

Finally, the osmotic pressure caused by a substance in very dilute solution is identical in value with the gaseous pressure which it would exhibit if the same quantity of it were contained as a gas in the same volume at the same temperature. For example, 44 g. of carbon dioxide in the gaseous condition fills the G.M.V. (22.4 l.), and at 0° exercises a pressure of one atmosphere. When we dissolve the same quantity of the same substance in 22.4 l. of any solvent at the same temperature, it causes approximately one atmosphere of osmotic pressure.

These facts apply to substances which are not acids, bases, nor salts. We shall learn in the next section that the osmotic pressures of the members of these three classes of substance are frequently abnormally high, but that the abnormality is easily explained.

Osmotic pressure (or suction) is a subject of great interest in connection with the physiology of plants and animals. The revival of a withered flower has been mentioned (p. 328). Similarly, the ascent of the water from the soil into the roots and through the stem of a growing plant is explained. In the animal body also, osmosis plays a large part.

**Osmotic Pressure and Dissociation in Solutions.** — What inference is to be drawn in the cases in which abnormally high osmotic pressures are observed? In view of the fact that the pressure depends on the fraction of foreign particles (molecules) in the given volume, we must infer that where the pressure is greater, more foreign particles are present in the given volume than we had supposed. In other words, dissociation of the original molecules must have occurred. This phenomenon is observed whenever acids, bases, or salts in aqueous solution are under observation. Thus a solution of sugar, which does not belong to these classes, containing 342 g. in the G.M.V., exhibits approximately the normal osmotic pressure of one atmosphere at 0°. A solution of one molecular weight of potassium chloride (74.5 g.) in the same volume of water, however, exhibits an osmotic pressure of about 1.88 atmospheres at 0°. The greater pressure must be due to the fact that, although the number of *molecules* of potassium chloride taken is the same as in the case

of sugar, the number of *actual particles* is greater, — is, in fact, 88 per cent greater. Now the multiplication of particles from potassium chloride molecules can occur only by their dissociation into particles of K and Cl by a chemical change represented by the equation  $\text{KCl} \rightleftharpoons \text{K} + \text{Cl}$ . In this case, seeing that each original molecule can give but two particles, the excess of pressure indicates that 0.88 (88 per cent) of the molecules of potassium chloride have been broken up. Comparison shows that the degree of dissociation for equi-molar solutions of different acids, bases, or salts varies widely. For the same substance, it is always relatively greater in dilute than in concentrated solutions.

It will be seen that we have thus a purely physical and perfectly independent confirmation of the indications already found in the chemical behavior of substances of this kind. In practice, on account of the experimental difficulties, this method is not used for measuring the degree of dissociation.

#### DEPRESSION IN THE FREEZING-POINT OF A SOLVENT

**Measurement of Freezing-Points.** — The task consists in measuring exactly the temperature at which a previously weighed quantity of the solvent freezes, and then, after dissolving in it a known weight of some soluble substance, determining the freezing-point once more. The absolute values of these two points are not required, it is simply the difference between them that has to be known with exactness (*cf.* p. 200). By means of a very delicate thermometer (Fig. 101) having only six degrees on the whole scale, the temperature of the freezing liquid may be read to one one-thousandth of a degree. A reservoir at the top enables us to add to, or subtract from, the mercury contained in the bulb and column, and so the same instrument may be used with solvents having widely different freezing-points. When water is being employed as the solvent, the outer

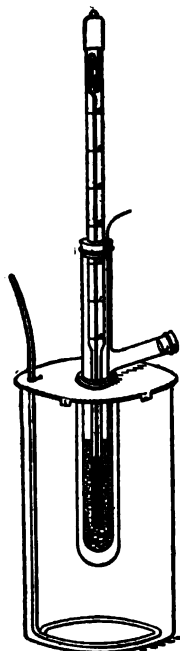


Fig. 101.

jar must be filled with a freezing mixture of ice and water containing salt. With solutions in benzene, ice and water are used alone. To avoid super-cooling the solvent or solution must be vigorously

stirred after it has been cooled down to a point just below the freezing-point.

**Laws of Freezing-Point Depression.**—The depression is directly proportional to the weight of dissolved substance in a given amount of the solvent. The depression is inversely proportional to the amount of solvent. Thus, if we double the concentration of the solution, the depression in the freezing-point is doubled. Further, equal numbers of molecules of different solutes in the same quantity of solvent give equal depressions. Or, in other words, the depression is proportional to the concentration of the molecules of the solute. Thus, solutions containing 342 g. of sugar ( $C_{12}H_{22}O_{11}$ ), or 46 g. of alcohol ( $C_2H_6O$ ), or 74 g. of methyl acetate ( $CH_3C_2H_5O_2$ ), in 1000 g. of water, show a depression below the freezing-point of water of  $1.86^\circ$  in each case, that is, such solutions will freeze close to  $-1.86^\circ$ . This depression produced by a mole of the solute in 1 l. of water is called the **molecular depression constant** and has a different value for each *solvent*. For solutions of the same molecular concentration in benzene (f.-p.  $5.48^\circ$ ) the depression is  $5^\circ$ , in phenol (carbolic acid)  $7.3^\circ$ . Combining these facts in one expression:

$$\left. \begin{array}{l} \text{The observed depression in an aqueous solution} \end{array} \right\} = 1.86^\circ \times \frac{\text{Wt. of Solute}}{\text{Mol. Wt. of Solute}} \times \frac{1000}{\text{Wt. of Solvent}}.$$

For other solvents, the corresponding value of the depression constant is substituted for  $1.86^\circ$ .

These principles may be expressed mathematically in a form which is convenient for use. If  $\Delta$  represent the depression in any actual experiment,  $\delta$  the depression produced by one molecular weight in 1000 grams of solvent,  $W$  the weight of the substance,  $M$  its molecular weight, and  $g$  the weight of the solvent in grams, then:

$$\Delta = \delta \times \frac{W \times 1000}{M \times g}.$$

In the case of water, as we have seen,  $\delta$  is  $1.86^\circ$ . For each solvent the value of  $\delta$  must be determined by means of a substance of known molecular weight.

These laws describe the facts most exactly when the solutions are dilute. They hold only when there is no chemical interaction between solute and solvent, and when the crystals frozen out consist of the pure solvent. If the crystals contain the same proportion of the solute as does the solution, no depression is observed: if they

contain *more*, an elevation in the freezing point is noted. Even so, however, acids, bases, and salts dissolved in water present many apparent exceptions and must be discussed separately.

**Determination of Molecular Weights.** — When the depression constant of a solvent has once been ascertained by means of a substance of known molecular weight, this method may be used for determining the molecular weight of other substances which are soluble in the same liquid. All the other factors can be observed and substituted in the formula. This method is especially useful when the substance cannot be converted into vapor without undergoing decomposition (see Hydrogen peroxide, p. 318).

**Abnormal Freezing-Point Depression: Dissociation in Solution.** — The substances which present the most conspicuous exceptions to the above rules are acids, bases, and salts in aqueous solution. With most of these, the depression produced is greater than we should expect from the concentration of the solution. Thus, in an actual experiment, two equi-molar solutions were compared. One contained one mole (74 g.) of methyl acetate, and the other one mole (58.5 g.) of sodium chloride, each dissolved in 2000 g. (2 liters) of water. The freezing-points observed, on the arbitrary scale of the thermometer, were:

Pure water . . . . .	3.580°	Pure water . . . . .	3.580°
Solution of methyl acetate .	2.610°	Solution of salt . . . .	1.902°
Depression . . . . .	0.970°	Depression . . . . .	1.678°
			0.970°
		Excess depression by salt	0.708°

The solution of methyl acetate, as it contained only 0.5 moles of the solute per liter of water, showed, as it should do, about half the average molecular depression (1.86°, p. 335). This is typical of the class of substances showing normal behavior. Sugar, alcohol, and hundreds of other substances, in solutions of the same molar concentration, would have given the same value.

The freezing-point of the salt solution, however, was much lower. If this solution had contained the same concentration of dissolved particles as the other solution, its depression would have been 0.970° likewise. The number of particles must therefore have been greater than we should have expected from the number of molecules taken. In other words, a portion of the molecules of the salt must have been

broken up, and the excess depression,  $0.708^{\circ}$ , must have been due to the *extra particles produced by dissociation*. Now sodium chloride molecules cannot give more than two particles each, and the depression is proportional to the number of particles. It follows, therefore, that  $\frac{1}{3}\frac{2}{3}$ , or 0.732 (73.2 per cent) of the molecules were dissociated:



This result is typical also. Acids, bases, and salts of which one mole is dissolved in two liters of water, are found to give irregular values, all more or less in excess of  $0.970^{\circ}$ . Those which contain but two radicals, like sodium chloride (NaCl) and potassium nitrate  $\text{KNO}_3$ , give values between  $0.970^{\circ}$  and  $2 \times 0.970^{\circ}$ . Substances like calcium chloride  $\text{CaCl}_2$  and sodium sulphate  $\text{Na}_2\text{SO}_4$  give depressions approaching three times the normal value: their molecules contain three radicals. The excess depression depends, therefore, upon the number of particles which each molecule can furnish, and upon the proportion of all the molecules which is dissociated into these fragments.

In the case of an acid, base, or salt, the depression is not strictly proportional to the concentration. Thus, one mole of salt in four liters of water does not give half the depression of the two-liter solution ( $0.839^{\circ}$ ) but *somewhat more* (about  $0.844^{\circ}$ ). The same method of calculation indicates, therefore, a greater degree of dissociation (about 79 per cent) in the more dilute solution. This dissociation, is, therefore, a reversible chemical change.

Acids, bases, and salts, so far as they are soluble in materials like toluene, benzene, chloroform, and carbon bisulphide, exhibit simply normal depressions in these solvents. It appears, therefore, that dissociation does not take place in many solvents. In common experience it is encountered only in solutions in water, and in alcohol.

**Abnormal Boiling-Point Elevation.** — If space permitted, a series of statements might be made in regard to the boiling-points of solutions (*cf.* p. 198) which would be closely parallel to those about freezing-points. The boiling-point, as we have seen, is elevated, however, by the introduction of a soluble body. Thus, when water is the solvent, one mole of a solute in 1000 g. of the solvent normally raises the boiling-point  $0.52^{\circ}$  (that is, from  $100^{\circ}$  to  $100.52^{\circ}$ ). One molecular weight of sodium chloride (58.5 g.), however, will elevate the boiling-point of the water  $0.87^{\circ}$  instead of  $0.52^{\circ}$ . The effect is  $0.35^{\circ}$ , or 67 per cent greater, indicating dissociation of this pro-



portion of the NaCl molecules. In more dilute solutions, the elevation is relatively greater. Salts containing more than two radicals, like  $\text{Ca}(\text{Cl})_2$ , give elevations of more than twice the normal value. In solvents like benzene and carbon disulphide, however, no abnormally large elevation is observed with any solute. The phenomena are, in fact, parallel with those connected with the freezing-point.

**Comparison of the Results of the Three Methods.** — When we measure the osmotic pressure, the freezing-point depression, and the elevation in the boiling-point of the same solution, and calculate the degree of dissociation from the result of each measurement, we find that the values obtained are usually identical, within the limits of error to which the methods are liable. Indeed, the theory of this subject enables us to connect the osmotic pressure by a mathematical relation with the other two phenomena, and to calculate any one of the three from any other. Thus the indications of dissociation found in the chemical behavior of acids, bases, and salts (p. 326) are fully confirmed by a study of the physical properties of their solutions.\*

The connection between the three sets of phenomena cannot be explained here. It is treated in all works on Physical Chemistry. It may be pointed out, however, that, in one essential respect, experiments in osmotic pressure, and in the freezing and boiling of solutions, are all alike. The perception of osmotic pressure involves a partition which the solvent alone can pass, and the osmotic pressure for a given solution is the one required to force the solvent out. In freezing a solution, pure ice is separated, and so a similar extrusion of a part of the pure solvent is effected. In a boiling solution, for which the above rules hold, the vapor is composed of the pure solvent, and the solute remains behind. The relation between the three operations lies in the fact that in each case the same thing, namely, the separation of a part of the solvent, is done. Each method effects this in a different way. But the expressions representing the work done, in terms of the factors which define the work in each case, can be equated in pairs and the required relation established. Thus the molecular depression of the freezing-point, or the molecular elevation in the boiling-point, as we have defined them, is equal to  $0.002 T^2 \div q$ , where  $T$  is the absolute temperature of the freezing- or boiling-point, and  $q$  is the heat of fusion or vaporization, as the case may be. Water, for example, freezes at  $273^\circ$  abs., and its heat of fusion is 79 cal. per gram, from which the calculated molecular depression,  $0.002 \times 273^2 \div 79$ , or  $1.88^\circ$ , is

\* Recent observations, showing that in some cases rapid double decompositions of the normal kind take place in solutions which exhibit no physical evidence of the existence of dissociation, demonstrate that it would have been unsafe to infer dissociation from chemical evidence alone.

obtained. Similarly, using the boiling-point,  $373^{\circ}$  abs., and the heat of vaporization of water, 540 cal. per gram, we calculate the molecular elevation of the boiling-point to be  $0.518^{\circ}$ .

It ought to be added that *abnormally small* osmotic pressures, freezing-point depressions, and boiling-point elevations, are also frequently observed. This occurs, however, almost wholly in non-aqueous solvents, such as benzene. It is shown particularly by substances containing oxygen, and is even noticed in the case of acids, bases, and salts. By parity of reasoning we infer that in these cases *association* (cf. p. 282) of the molecules has occurred, and that the physical unit of the solute in these solvents is larger than the ordinary molecule.

### THE APPLICATION OF THESE CONCLUSIONS IN CHEMISTRY

#### *The Constitution of Solutions of Acids, Bases, and Salts.*

— The composition of solutions which are normal or abnormal, in respect to osmotic pressure, freezing-point, and boiling-point, may be shown thus:

SOLUTES.	DISSOLVED IN WATER, ALCOHOL, ETC.	DISSOLVED IN TOLUENE, CHLOROFORM, ETC.
Acids, bases, salts . . . . .	Abnormal	Normal
Other substances . . . . .	Normal	Normal

It appears that water and some other solvents have the power of decomposing acids, bases, and salts. Such solvents have, in fact, an effect on these materials that resembles, outwardly at least, the effect which heat has on many substances (cf. p. 260), **they cause dissociation:**



In consequence of this, our view of the nature of an aqueous solution of hydrogen chloride HCl, or common salt NaCl, or sodium hydroxide NaOH, or any of the substances of the classes which these represent, may now be stated in definite terms. Such a solution contains, besides undivided molecules of the solute, at least two other kinds of material, H, Na,\* Cl, OH, etc., which result from the breaking up of the molecules. We shall see that these subdivisions of the original molecules have distinct physical and chemical properties of their own. The descriptions of the "properties" of the solutions, as

\* The objection that separate atoms of sodium could not remain free in water, will be disposed of later.

they used to be given in chemistry, were really a confused statement of the properties of the different components of a mixture.

The suggestion that the multiplication of particles takes place by interaction of the salt with part of the water,  $\text{NaCl} + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{HCl}$ , resulting in the production of two molecules of dissolved matter from one, is open to several fatal objections. In the case of a highly dissociated salt, according to this explanation, the mixing of the acid and base in dilute solution should result in no particular change and give rise, therefore, to no development of heat. But the heat of neutralization is very great in such cases. This is an example of a stochastic hypothesis (p. 176), be it noted, and its verity or falsity can be put to the test at once. Its inapplicability is further seen in the fact that it cannot explain the dissociation of acids and bases themselves.

The *free radicals*, of whose existence we have thus become convinced, constitute a new set of materials (with appropriate names. See p. 356). Thus the hydrogen radical of acids, although a form of uncombined hydrogen, differs totally from the gas which is composed of the same material. The gas has no sour taste or effect upon litmus; these are properties of the free radical. The gas is very slightly soluble in water, while the hydrogen radical exists as a separate substance only in solution. Again, substances with the composition of the radicals  $\text{NO}_2$  and  $\text{SO}_4$  are not known at all except in solutions. The chief peculiarity of these substances is that a solution cannot be made which contains less than two kinds of them side by side.

**Exercises.** — 1. What gaseous pressure would be exerted by a gas of the same molecular concentration as a one per cent solution of sugar at  $15^\circ$  (p. 331)? Compare the answer with the osmotic pressure of the solution.

2. What depression in the f.-p. of water will be produced by dissolving 10 g. of bromine in 1 kg. of this solvent?

3. What depressions in the f.-p. of benzene and of phenol would be produced by 10 g. of bromine to 1 kg. of the solvent, if no chemical action took place?

4. What is the molecular depression-constant of a solvent in which 5 g. of iodine in 500 g. of the solvent lowers the f.-p.  $0.7^\circ$ ?

5. What is the degree of dissociation of zinc sulphate if 5 g. of it dissolved in 125 g. of water produce a lowering of  $0.603^\circ$  in the f.-p.? What is the molecular concentration of each of the four substances present in this solution?

6. What will be the approximate b.-p. of a solution of common salt, saturated at  $100^{\circ}$  (p. 191)? Assume that the solute is 50 per cent dissociated.

7. In a decinormal solution, potassium chloride is 86 per cent dissociated. What is the freezing-point of this solution?

8. If 5 g. of a substance, dissolved in 1000 c.c. of water, give a solution freezing at  $-0.2^{\circ}$ , what is the molecular weight of the substance?

9. 6 g. of a substance when dissolved in 200 c.c. of water give a boiling-point of  $102.6^{\circ}$ . What is the molecular weight of the substance?

10. 1.6 g. of naphthalene  $C_{10}H_8$  when dissolved in 25 g. of benzene (freezing-point  $5.48^{\circ}$ ) gives a solution which freezes at  $3.03^{\circ}$ . When 2.44 g. of another substance are dissolved in the same amount of benzene, the solution freezes at  $3.52^{\circ}$ . What is the molecular weight of the latter substance?

11. The elevation of the boiling-point in the above solution of naphthalene is  $1.285^{\circ}$ . What elevation of the boiling-point is produced in the second solution?

## CHAPTER XVIII

### IONIZATION

**Introductory.** — As we have seen, acids, bases, and salts, when dissolved in water, interact with one another by *interchanging radicals* (p. 324). We have also learned that the same solutions have abnormal values for their freezing-points, boiling-points, and osmotic pressures. These facts indicate *dissociation into the radicals* (p. 339). Now **precisely these solutions have a property** which is not shared by any other solutions, namely, that of being **conductors of electricity and suffering chemical decomposition by the passage of the current**. Such solutions are called, in consequence, **electrolytes**, and the process is named **electrolysis**. Now the natural inference from the foregoing facts is that **the electricity is carried by the liberated radicals**. Our first aim in the present chapter is to show, by a study of the **chemical changes taking place in electrolysis**, that this inference is correct. We then proceed to discuss the **nature of ions as a kind of molecules**. Next, we devote ourselves to the **explanation of electrolysis, to the equilibrium between the ions and the remaining, undissociated molecules, and to conductivity phenomena** as a means of measuring the **fraction ionized**. Finally, we deduce the relation between extent of ionization and **chemical activity**.

Incidentally, the facts to be given provide the means of understanding the electrolytic processes, many of them of great importance in chemical industries, to which frequent reference is made in later chapters.

**Non-Electrolytes.** — To clear the ground, we should first note the fact that only solutions (as a rule) possess both of the properties in question, namely that of conducting and that of being decomposed by the current. Some substances, notably the metals and materials like carbon, are conductors. But they are not changed chemically by the current. Again, single substances, even when they are such as, if mixed, yield electrolytes, are not conductors at ordinary temperatures. Thus hydrogen chloride, whether gaseous

or liquefied, is a nonconductor, and water is a very feeble conductor, although the solution of the two conducts exceedingly well. Dry acids, bases, and salts, except when at a high temperature and fused, are likewise nonconductors. Furthermore, even amongst solutions, not all are conductors. Solutions of sugar and other substances of the same class (p. 335), which have normal freezing-points, are nonconductors. Only solutions of acids, bases, and salts in certain specified solvents, of which the commonest is water, are electrolytes at ordinary temperatures.

**Chemical Changes Taking Place at the Electrodes During Electrolysis.**—When the wires from a battery are attached to platinum plates immersed in any electrolyte (*e.g.*, Fig. 87, p. 216, or Fig. 16, p. 29), we observe that the products appearing at the two electrodes are always different. They may be of several kinds physically, and will be secured for examination variously according to their nature. When they are **gases**, which are not too soluble, they may be collected in inverted tubes filled with the solution. **Solids**, if insoluble in the liquid, will either remain attached to the electrode or fall to the bottom of the vessel as precipitates. **Soluble substances**, on the other hand, will usually not be visible. They may be handled by interposing a porous partition of some description which will restrain the diffusion of the dissolved body away from the neighborhood of the electrode, while not interfering appreciably with the passage of the current. Surrounding one electrode with a porous battery jar is a convenient method for effecting this.

Of the various illustrations which we have encountered, the electrolysis of hydrochloric acid (p. 216) happens to have been the only one which delivered both components of the solute with a minimum of modification at the electrodes:



Hydrogen does not interact with water, and chlorine interacts very incompletely, so that the molecular substances  $\text{H}_2$  and  $\text{Cl}_2$  are promptly formed from the elements H and Cl which are liberated. The chlorides, bromides, and iodides of those metals which do not interact with water (p. 129) give equally simple results:



Thus the solute seems to be *split into its radicals*, and in electrolysis, the radicals, if they do not interact with water, are set free. A

substance thus set free is called a **primary product** of the electrolysis. In the foregoing instances both products are primary.

Usually the chemical change is more complex. Thus, when dilute sulphuric acid is electrolyzed, hydrogen and oxygen are liberated at the negative and positive electrodes, respectively. But these products do not account for the whole of the constituents ( $\text{H}_2\text{SO}_4$ ). We therefore proceed to examine the materials in solution round the electrodes. It is found that, as the action progresses, sulphuric acid accumulates round the positive wire, while the liquid in the neighborhood of the other pole is gradually depleted of this substance. In view of this fact we easily explain the phenomenon. Evidently the substance divides into its radicals, H and  $\text{SO}_4$ , but the  $\text{SO}_4$  must interact with the water to produce sulphuric acid and oxygen:  $2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4 + \text{O}_2$ . The whole change may therefore be tabulated as follows:

Neg. Wire,  $\text{H}_2 \leftarrow \text{H}_2\text{SO}_4 \rightarrow \text{O}_2$  and  $\text{H}_2\text{SO}_4$ , Pos. Wire.

Hence the hydrogen is a primary product, but the oxygen and sulphuric acid are **secondary products**. All acids give hydrogen alone at the negative electrode, whatever may be the product at the positive.

If we electrolyze cupric nitrate solution, we obtain a red deposit of metallic copper on the negative plate and at the positive end oxygen and nitric acid are formed. We infer, therefore, that the division of the original molecule was into Cu and  $\text{NO}_3$ , but that the latter interacted with the water:  $4\text{NO}_3 + 2\text{H}_2\text{O} \rightarrow 4\text{HNO}_3 + \text{O}_2$ :

Neg. Wire,  $\text{Cu} \leftarrow \text{Cu}(\text{NO}_3)_2 \rightarrow \text{O}_2$  and  $\text{HNO}_3$ , Pos. Wire.

With a solution of potassium chloride we find hydrogen and chlorine appearing at the negative and positive electrodes, respectively. Litmus paper, however, shows the presence in the solution of a base (potassium hydroxide, KOH) at the negative end. We infer that the parts of the parent molecules are K and Cl. The former, since it resembles sodium in being much more active than hydrogen (p. 216), is more difficult to liberate. Hence hydrogen is liberated instead, and potassium hydroxide remains in the liquid:  $2\text{K} + 2\text{HOH} \rightarrow 2\text{KOH} + \text{H}_2$ :

Neg. Wire,  $\text{H}_2$  and KOH  $\leftarrow \text{KCl} \rightarrow \text{Cl}_2$ , Pos. Wire.

We are confirmed in this explanation when we employ a solution

containing a *mixture* of salts of copper and silver. The latter, being the less active metal, is first deposited, alone. The copper is liberated only after all the silver has been set free.

Having now before us the results of electrolyzing some typical substances, we bring these results into relation with the facts described in Chapter XVII. Acids contain hydrogen which possesses certain specific properties (p. 324), and in electrolysis all acids divide so as to give up *this constituent alone* at one electrode. The evidence that the other radical has different electrical properties which carry it to the opposite plate is conclusive. Again, salts undergo double decomposition in which they exchange radicals with acids, bases, and other salts (p. 324), and we find that it is **these very radicals which are withdrawn from the solution by the influence of the electricity**. Furthermore, the radicals exist free in the solution, being formed by dissociation of the molecules (p. 339). Hence **the function of the electricity seems simply to consist in sifting apart the two kinds of free radicals** which each solution contains. It only remains for us to explain in detail the sifting action of the current. Before turning to this explanation of the phenomena, however, there is one question which may be answered in passing. Since a solution may eventually be cleared of all the hydrochloric acid, for example, which it contains, we should like to know how the free radicals in the center of the cell reach the electrodes.

**Ionic Migration.**—To know how the free radicals reach the electrodes, all that is necessary is to take a material, one (or both) of whose radicals is a colored substance, and watch the movement of the colored material as it drifts towards the electrode. Most salts that give colored solutions are suitable. In dilute cupric sulphate solution, for example, a freezing-point determination shows that the depression has practically double the normal value. In other words, the dissociation into the radicals,  $\text{CuSO}_4 \rightleftharpoons (\text{Cu}) + (\text{SO}_4)$ , is almost complete. Now, the blue color of this solution cannot be due to the remaining molecules of  $\text{CuSO}_4$ , for anhydrous cupric sulphate is colorless. Nor is it due to the color of the  $(\text{SO}_4)$  radicals, for dilute potassium sulphate and dilute sulphuric acid are both colorless. On the other hand, all cupric salts, in dilute solution, have the same tint. The color is therefore that of the free cupric radical  $(\text{Cu})$ . In order most clearly to see the motion of the cupric radical, we place the cupric sulphate solution in the middle of the space between the electrodes, and place between it and the latter a colorless conducting



solution. The motion of the blue material across the boundary may then be easily observed.

The most convenient arrangement is to dissolve the cupric sulphate in warm water containing about 5 per cent of agar-agar (a

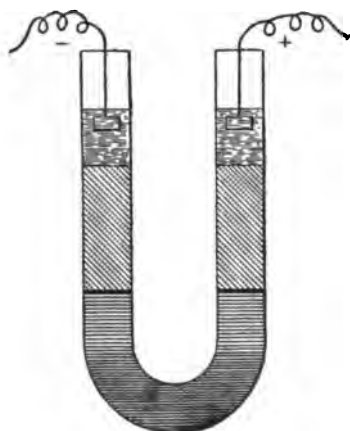


FIG. 102.

gelatine obtained in China from certain sea-weeds), and to fill with this mixture the lower part of a U-tube (Fig. 102). The setting of the jelly prevents subsequent mixing of the cupric sulphate system of materials with the rest of the filling of the tube, and the consequent disappearance of the boundary. A few grains of charcoal are scattered on the surface of the jelly to mark the present limits of the colored substance, and a solution of some colorless electrolyte, such as potassium nitrate, is added on each side. To prevent agitation of the liquid by the effervescence at the electrodes, it is well to use agar-agar

with the lower part of the colorless liquid also. The whole is finally placed in ice and water, to prevent melting of the jelly by the heat caused by resistance, and the current is then turned on. The agar-agar does not offer any appreciable resistance to the motion of the ions, and is presumed to form a sort of open network in the solution.

After a time, we observe that the blue cupric ions ascend above the mark on the negative and descend away from it on the positive side. In each case there is no shading off in the tint. The motion of the whole aggregate of colored radicals occurs in such a way that, if the contents of the tube were not held in place by the jelly, we should believe that a gradual motion of the entire blue solution was being observed. With a current of 110 volts, and a 50-watt lamp (one-half ampere) in series with the cell, the effect becomes apparent in a few minutes.

Although the  $(SO_4)$  radicals are invisible, we may safely infer that they are drifting towards the positive electrode. Indeed, this can be demonstrated by interposing a shallow layer of jelly containing some barium salt a little distance above the charcoal layer on the positive side. When the  $(SO_4)$  radicals reach this, barium sulphate begins to

be precipitated and the layer becomes cloudy. In similar ways the progress of other colorless ions may be rendered visible.

It appears therefore that electrolysis is not a local phenomenon, going on round the electrodes only, but that the whole of the products of the dissociation of the solute are set in motion. It is on account of this remarkable property of traveling or migrating towards one or other of the electrodes connected with a battery that the individual atoms (like Cu), or groups of atoms (like  $\text{SO}_4$ ) have been named ions (Gk. *ion*, going). The term was first applied by Faraday to the materials liberated round the electrodes.

Some writers use the word "wandering" for migration. But wandering means rambling without any certain course or object in view, like diffusion of a gas. The ions move like a disciplined regiment, with a straight front, and exactly equal speed along that front. Migration is the movement of a population in a definite direction, and is, therefore, the appropriate term. The error is due to ignorance of German, in which language *Wandering* means migration and not wandering.

**Relative Speeds of Migration of Different Ions.** — The speeds of different ions may readily be compared. The cupric ion moves at the same speed whatever salt of copper we employ. In fact, the speeds of all ions are individual properties and are independent of the nature of other ions that may be present. The speeds of all are increased by using a current of greater electromotive force. Under similar conditions, the relative speeds of most ions are in the neighborhood of 50 or 60, on the scale commonly used in expressing ionic velocities. Thus, we have (K) 65.3, (Cl) 65.9, (Cu) 49. The speed of the hydrogen ion of acids is the greatest of all, 318, while that of hydroxide ion of bases (OH) comes next, being 174. These are, respectively, about five and two and one-half times as fast as any other ions.

The actual speeds of these ions in dilute solutions at  $18^\circ$ , when driven by a potential difference of 1 volt between plates 1 cm. apart, expressed in cm. per hour is: (K) 2.05, (Cl) 2.12, (Cu) 1.6, (H) 10.8, (OH) 5.6, ( $\text{SO}_4$ ) 1.6.

By an experiment similar to the last, and devised by A. A. Noyes, the relative speeds of different ions may be demonstrated. The U-tube (Fig. 103, showing the same tube *A* before the current starts, and *B* after it has been passing for some time) is partly filled with agar-agar emulsion containing potassium chloride and phenolphthalein (see Indicators). On the right side, a drop of potassium hydroxide has been added to render the mixture pink. On the left, a drop of hydro-

chloric acid is present, and the mixture is colorless. Above the charcoal layer, in the right limb, a mixture of hydrochloric acid and cupric chloride, i.e.,  $H^+$  and  $Cu^{++}$ , and in the left limb potassium hydroxide solution, i.e.,  $OH^-$ , are placed. The positive electrode is introduced on the right and the negative on the left. The  $H$  and  $Cu$  ions drift away from the former down the tube towards the latter, the  $OH$  ions away from the latter down the tube towards the former. The motion

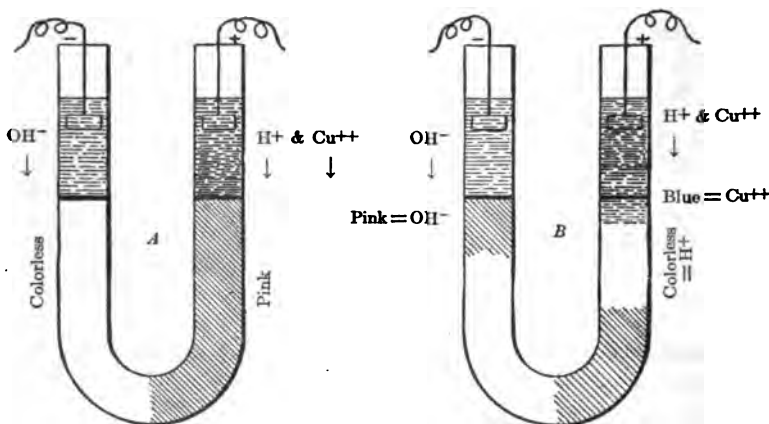


FIG. 103.

of the  $H$  is marked by the disappearance of the pink color, that of the  $Cu$  by the advance of a blue layer, that of the  $OH$  by the progress of a pink coloration.\* By the time the  $H$  ions have been displaced  $5\frac{1}{2}$  cm., the  $Cu$  ions have moved 1 cm. and the  $OH$  about  $2\frac{1}{2}$  cm. These distances indicate their relative speeds of migration.

**The Nature of Ions.** — That the molecules of certain classes of substances, although seemingly without chemical interaction with the water in which they are dissolved, should nevertheless be decomposed by the influence of the water, is strange, but not inconceivable. Heating produces a somewhat similar effect on many substances. There are two peculiarities to be accounted for:

How can the production of a conducting medium by mixing two nonconductors be imagined to take place? The solvent is a non-conductor, and the ions, even if they are composed of conducting

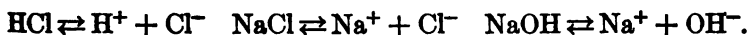
\* Bases, on account of the  $(OH)$  they give, turn phenolphthalein solutions from colorless to pink; acids, on account of the  $(H)$  they furnish, turn it from pink to colorless (see Indicators).

material, are distributed through the liquid as independent particles and cannot furnish a continuous medium for the stream of electricity. This will be clear when we remember that although liquid mercury is an excellent conductor, mercury vapor, composed as it is of conducting particles, is not a conductor.

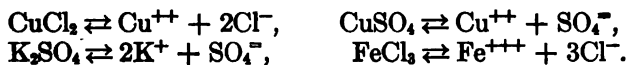
Again, the conducting power of the solution is indissolubly connected with the fact that the original molecules of the solute have been broken up by the solvent into smaller molecules containing one or more atoms. Why should this particular kind of sub-molecules be attracted by electrically charged plates, which have been lowered into the solution, when molecules of dissolved sugar, for example, are not so attracted?

An answer to the second question readily suggests itself. The only bodies which we find to be conspicuously attracted by electrically charged objects are bodies which are *already provided with electric charges of their own*. Thus we are led to add the idea that substances which undergo dissociation in solution **divide themselves into a special kind of electrically charged molecules**.

Since the solution, as a whole, has itself no charge, **equal quantities of positive and negative electricity must be produced**:



Wild as this supposition seems at first sight to be, it turns out that no valid objection to it can be raised. This means that bivalent radicals, on dissociation, will become ions carrying a double charge and trivalent ions must carry a triple charge:



In these equations, the coefficients multiply the charges as well as the radicals bearing the charges, and it will be seen that the numbers of + and - charges produced by each dissociation are equal. Hence, **univalent ions all possess equal quantities of electricity, and other ions bear quantities greater than this in proportion to their valence**. This is an inevitable inference from the electrical neutrality of all solutions. An ion is therefore **an atom or group of atoms bearing an electric charge**.

To show that this view of the nature of the ions is adequate, after a section on Faraday's law, we shall next apply it to the explanation of the phenomena of electrolysis. After that some seeming objections will be discussed.

**Faraday's Law.** — The above conclusion is confirmed by actual measurement. Quantitative experiments in electrolysis show the most perfect adjustment in this respect. Thus, in a single cell, the quantities of material liberated at the two poles are invariably chemical equivalents of one another. With hydrochloric acid, while 1.008 g. of hydrogen are being liberated at one pole, 35.46 g. of chlorine are set free in the same time at the other. But when cupric chloride  $\text{CuCl}_2$  is substituted, for every 35.46 g. ( $= \text{Cl}$ ) of chlorine set free, only 31.78 g. ( $= \frac{1}{2} \text{Cu} = \frac{1}{2} 63.57$ ) of copper are deposited.

Again, the amount of any one substance liberated is proportional to the quantity of electricity which has traversed the cell. This is the first part of Faraday's law.

Finally, the passage of equal quantities of electricity through several different acids liberates equal amounts of hydrogen from each. This is true, whether the passage of the given quantity of electricity is compressed into a brief time in one case and spread over a longer time in another, or is uniform in all cases compared. It is irrespective of the state of dilution and of the temperature of each acid. Thus two moles of hydrochloric acid  $\text{HCl}$  are always decomposed for every one of sulphuric acid  $\text{H}_2\text{SO}_4$  by the same current. Similarly, if in different cells we place solutions of substances like sodium chloride  $\text{NaCl}$ , cupric chloride  $\text{CuCl}_2$ , antimony chloride  $\text{SbCl}_3$ , ferrous chloride  $\text{FeCl}_2$ , and ferric chloride  $\text{FeCl}_3$ , equal amounts of chlorine are liberated by currents of equal strength in the same time in each.

If we consider the relation of these facts to the equivalence of the materials liberated in any one cell, it will be evident that when one gram of hydrogen is liberated from each of the two acids mentioned above, one equivalent of chlorine will be set free in the one cell, and one equivalent of  $\text{SO}_4$ , or half the weight represented by the formula, will be set free in the other. Similarly, with the chlorides of the second and third metals, while 35.46 g. of chlorine are being liberated in each cell, the quantities of the metal set free will be, of copper one-half of 63.57 g., and of antimony one-third of 120.2 g. Finally, with the two iron salts, the quantities of iron liberated by the same current will be one-half and one-third of 55.84 grams, respectively.

The simplest way in which to insure the passage of precisely equal amounts of electricity through all the cells is to arrange them in series. We know that in such circumstances the quantity of electricity traversing any section of the whole circuit must be the same as that traversing any other. In a series of cells containing substances like the above, therefore, during the time that 1.008 g. of hydrogen is

being set free, we shall have liberation of the equivalent quantities of each of the other ions (Fig. 104). Thus the second part of Faraday's law states that: **Equal quantities of electricity liberate chemically equivalent quantities of the ions** (equivalent, p. 63, not atomic or molecular).

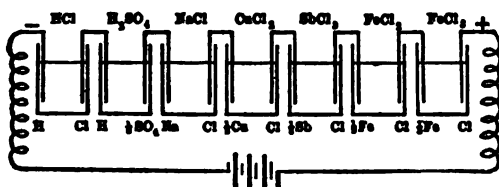


FIG. 104.

In this connection we note that the ionizations of ferrous chloride and of ferric chloride are written as follows:



Ferrous-ion  $\text{Fe}^{++}$  and ferric-ion  $\text{Fe}^{+++}$ , although differing only in the quantity of the charge carried by each ion, have entirely distinct chemical properties. In writing equations involving ions, care must always be taken to make the numbers of + and - charges equal.

**Application: The Explanation of Electrolysis.** — A battery is a machine which maintains two points, its poles, or two wires connected with them, at a constant difference of potential. One cell of a lead storage battery, for example, maintains a potential difference of about two volts. When the wires are joined, directly or indirectly, the poles are immediately discharged, but the cell continuously reproduces the difference in potential by generating fresh electricity. Now the effect of immersing two plates, one of which is kept by the battery at a definite positive potential and the other at a definite negative potential, into a liquid filled with floating multitudes of minute bodies, *already highly charged*, may easily be foreseen.

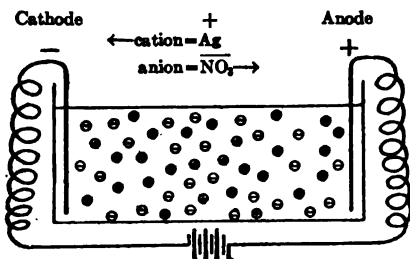


FIG. 105.

The figure (Fig. 105) will convey some idea of the behavior of the parts of a system such as we have imagined. The electrodes are marked - and +. The negatively charged plate attracts all the positively charged particles in the vessel and, although these particles were in continuous and irregular motion, they at once begin to drift toward the plate in question. On the other hand, the negatively charged particles are repelled by this plate and attracted by the positive plate, so that they drift in the opposite direction. Those which are nearest each plate, on coming in contact with it, will lose their charges of electricity, turning thereby into the ordinary free forms of the matter of which they are composed. The continuous removal of the electrical charges of the plates through contact with ions of the opposite charge furnishes occasion for recharging of the plate from the battery, and thus gives rise to a continuous current in each wire. Again, the continuous drifting of positively and negatively charged particles in opposite directions through the liquid constitutes what, in the view of all external means of observation appears to be an electrical current in the liquid also. A magnetized needle, for example, which is deflected when brought near one of the wires of the battery, is influenced in the same way by being brought over the liquid between the electrodes. The illusion, so to speak, of an electric *current* is complete, although in reality it is a *convection* of electricity that is taking place. Furthermore, the quantity of electricity being transported across any section of the whole system is the same as that across any other, whether this section be taken through one of the wires, through the electrolyte, or even through the battery at any point. As fast as the ions are thus annihilated as such, the undissociated molecules (mingled with the ions, but not shown in the figure) dissociate and produce fresh ones, as in all chemical equilibria. Eventually, by continuing the process long enough, if the substance set free are actually deposited and do not go into solution again in any form, the liquid can be *entirely* deprived of the solute which it contains.

The analogy to the transportation of a fluid like water is noticeable although not complete. Water may be transported in three ways. It may flow through a pipe, it may pass by pouring freely from one container to another, and it may be carried in vessels. Thus a stream of water, essentially continuous, might be arranged, in which part of the passage took place through the pipes, part by pouring from the pipes into buckets, and part by the carrying of those buckets between the ends of the pipes. The quantity of water passing a given point per minute in this system would be the same at every part, although the

actual method by which the water was transported past the various points might be different. In such a disjointed circuit we suppose the electricity to move when carried from a battery through an electrolytic cell. It flows in the wire, passes by discharge between the pole and the ion, and is transported upon the ions in the liquid. The parallel is imperfect, however, because we have used the conception of *two electric fluids* and *because the ions are already charged in the solution, and before any connection with the battery is made*. They do not, so to speak, transport the electricity of the battery, but their own.

The harmony between the quantity of electricity and the chemical valence of the material which it liberates is complete. The picture which the process of electrolysis in a series of cells (p. 351) presents to our minds is very interesting. The progress of the electricity through the series is accompanied by a simultaneous discharge in all the cells of chemically corresponding numbers of ions. For every atom of antimony that is liberated in one cell, three atoms of chlorine, three atoms of hydrogen, and one atom of ferric iron, are set free at the same time. For two atoms of ferric iron, three atoms of ferrous iron and three atoms of copper are deposited. Even in the battery which generates the current, the chemical changes taking place proceed atom for atom and valence for valence in unison with those in the cells on the circuit. For example, if the battery contains zinc plates, for every atom of zinc that dissolves, one of copper and two of chlorine will be liberated in one of the cells. Our imaginary mechanism thus puts all the processes going on in the circuit in the light of movements of the parts of a perfectly adjusted and interlocked machine.

**Questions Suggested by this Explanation.** — The question was raised (p. 339), as to how we can imagine separate atoms of sodium to exist in water without acting upon it, as the metal sodium usually does. But the ions of sodium in sodium chloride solution are *not* metallic sodium. They bear large charges of electricity. They possess an entirely different, and in fact, by measurement, much smaller amount of chemical energy than free sodium. And the properties of a substance are determined as much by the energy it contains as by the kind of matter. Metallic sodium and ionic sodium are, simply, different substances.

Besides, when metallic sodium acts on water, it turns into the ionic sodium of sodium hydroxide (p. 115):  $\text{Na}^+ + \text{OH}^- \rightleftharpoons \text{NaOH}$ . Ionic sodium  $\text{Na}^+$  from sodium chloride is, therefore, *already in*



the very state which metallic sodium reaches by interaction with water, and is in no need of trying to enter that state.

2. We think of hydrogen chloride and common salt as exceedingly stable substances, and are averse to believing that precisely these compounds should be highly dissociated by mere solution in water. But it must be remembered that in solution they undergo chemical change very easily, and it is only in the dry form that they show unusual stability.

3. Again, why do not the ions combine, in response to the attractions of their charges? The answer is that they do combine, but the rate at which combination takes place is no greater than that at which the molecules decompose, so that on the whole the proportion of ions to molecules remains unchanged.

4. It might appear that the idea that bodies could retain high charges in the midst of water is contrary to all experience. It must be remembered, however, that the molecular, pure water, which separates the ions from one another, is a perfect nonconductor. The moisture which covers electrical apparatus and causes leakage of static electricity is not pure water, but a dilute solution containing carbonic acid (p. 197) and materials from the glass of which the apparatus is made (p. 143). It conducts away the charge electrolytically, by means of the ions it contains, and not by itself acting as a conductor.

5. Finally, when we dissolve an electrically neutral salt in water, whence do the radicals obtain the electric charges? We now know that an atom, say of sodium, contains a minute nucleus of positive electricity, which contains most of the mass of the atom. Outside of this nucleus, there are particles of negative electricity, called **electrons** (*q.v.*), each having a mass about one-seventeen hundredth ( $\frac{1}{1700}$ ) of that of an atom of hydrogen. An ion of chlorine ( $\text{Cl}^-$ ) consists, therefore, of an atom of chlorine *plus* one electron ( $\text{Cl} + e$ ). An ion of sodium is an atom of sodium *minus* one electron ( $\text{Na} - e$ ) and has thus an excess of one unit positive charge in the nucleus. When these two ions combine, the resulting molecule  $\text{NaCl}$  is neutral.

According to this view, a **battery is a source of electrons**, which pass in a stream along the negative wire. When the electrons reach the electrode in an **electrolytic cell**, they (being negative) attract the positively charged ions and, when the latter touch the electrode, the missing one or more electrons are supplied to each ion, and the material of the ion is then neutral and free:



The negative ions are repelled by the negative electrode and move toward the positive one. Also, if several positive ions could be rendered neutral and free, there would be an excess of negative charges in the solution. To avoid this, the negative ions in contact with the positive electrode give up an equivalent number of electrons to the plate and wire:  $2\text{Cl}^- \rightarrow \text{Cl}_2 \uparrow + 2e$ . Thus, the circulation of the electrons is completed, and the current of electrons flows in all parts of the system.

**Résumé and Nomenclature.** — The dissociation of molecules into ions is named **ionization**. The substances of the three classes which alone are ionized are designated **ionogens**. An **ion** may be defined as a molecule bearing negative or positive charges of electricity in proportion to its valence, and formed through the dissociation of an ionogen by a solvent like water.

The solution of an ionized substance is called an electrolyte, and often this term is applied also to acids, bases, and salts themselves, because, when dissolved, they produce electrolytes. This is rather a confusing metonymy, however, because these bodies by themselves are *not conductors*. This use of the term also introduces obscurity because it connects the ionization with electrolysis and always conveys the impression that the latter produces the former. The electrolytic property of ions is only one amongst many special properties of electrolytes, and the majority of these properties are chemical and have nothing to do with electrolysis. Hence we have preferred the more general word "ionogen."

Each molecule of the solute gives two kinds of ions with opposite charges. These two are forthwith distinct and independent substances, save that the attractions of the charges prevent any considerable separation by diffusion. They differ from non-ionic substances of the same material composition when such are known. The electrical charge is one of the essential constituents and, when it is removed, the properties alter entirely. Thus we have two kinds of hydrogen — gaseous, molecular hydrogen ( $\text{H}_2$ ), and ionic hydrogen ( $\text{H}^+$ ) — with entirely different chemical properties (p. 340).

The radicals and their chemical behavior are real, and all the peculiarities of aqueous solutions of acids, bases, and salts are experimental facts. We now have experimental knowledge of the minute parts of bodies. Molecules are units which are not commonly disintegrated by vaporization (p. 233); ions, those which are not commonly disintegrated in double decomposition in solution; atoms, those which are not commonly disintegrated in any chemical action. But there are exceptions in each of the three cases. The ionic

explanation was first suggested as an hypothesis by Svante Arrhenius, a Swedish chemist, in 1887. From the appearance of his remarkable memoir we date the great development which the study of solutions\* has undergone in recent years.

It is worth noting that the quantities expressed by the formulæ Al, Ca, and K, when existing as ions, produce equal osmotic pressures, and have equal effects upon the freezing- and boiling-points. This is a further justification for our choice of chemical unit quantities of the elements (atomic weights), for the atomic weights have these properties in common, and equivalents, of course, do not (*cf.* p. 245).

Since ionic hydrogen, ionic chlorine, etc., are entirely different in physical and chemical properties from the corresponding free elements, they should receive separate names. When it is inconvenient to say "ionic hydrogen," "ionic nitrate radical" ( $\text{NO}_3^-$ ), etc., the following names will be used for the ionic substances:

Symbol.	Name of Substance.	Anion of	Symbol.	Name of Substance.	Cation of Salts of
$\text{SO}_4^{--}$	Sulphate-ion	Sulphates	$\text{Na}^+$	Sodium-ion	Sodium
$\text{Cl}^-$	Chloride-ion	Chlorides	$\text{Fe}^{+++}$	Ferric-ion	Ferric iron
$\text{FSO}_4^-$	Hydrosulphate-ion	Bisulphates	$\text{NH}_4^+$	Ammonium-ion	Ammonium
$\text{OH}^-$	Hydroxide-ion	Hydroxides (bases)	$\text{Fe}^{++}$	Ferrous-ion	Ferrous iron
		"	$\text{H}^+$	Hydrogen-ion	Hydrogen (acids)

In using these terms, note that sodium-ion (with the hyphen) is the name of the *substance*, and not of the charged atom. When speaking in terms of ions as particles, therefore, we may not say "a sodium-ion," any more than we should say "an ionic sodium" or "ionic sodiums." To describe the charged molecule, we must write "a sodium ion," "sodium ions," "chlorate ions," etc.

Faraday distinguished by name the two kinds of material which proceed with and against the positive current. His terminology is still used. Ions which proceed in the same direction as the positive current (Fig. 105, p. 351) are called **cations** (Gk. *κατά*, down). Such are  $\text{H}^+$ ,  $\text{Cu}^{++}$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ . They are **metallic elements**, or groups which play the part of a metal. The electrode (Gk. *ὁδός*, a path) upon which they are deposited, the negative electrode, is spoken of as the **cathode** (Gk. *ἡ καθόδός*, the way down).

\* The *Scientific Memoirs*, No. IV (American Book Company), is a reprint of the fundamental papers by Raoult, van't Hoff, and Arrhenius.

The particles which move in the direction of the negative current, and against that of the positive, are named **anions** (Gk. ἀνά, up). The ions  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{--}$ ,  $\text{MnO}_4^-$  are of this kind. They are usually composed of **non-metals**, although sometimes, as in  $\text{MnO}_4^-$ , the constituents may be partially metallic. They are set free at the positive electrode, which is therefore named the **anode** (Gk. ἀνόδος, the way up). Chemists speak of metallic and non-metallic elements as **positive** and **negative elements**, respectively (cf. p. 150), even when electrical relations are not directly in question, and ions are not concerned.

In order that this idea may be carried out consistently, the liberation of any of these ionic materials at one electrode in electrolysis is written as follows:



Here  $\ominus$  and  $\oplus$  represent the unit quantities of negative and positive electricity furnished by the battery to the electrodes and destroyed by opposite charges upon the ions.

The solvents which produce ionization are the associated liquids (p. 282), like water (p. 202), liquefied ammonia, and alcohol. Those which do not produce ionization are the non-associated liquids, like benzene, toluene, and carbon disulphide. This likewise is explained by the fact that the former have, by measurement, high dielectric constants, and so are able to hold charged bodies apart, while the latter have low ones.

**Actual Quantities of Electricity Concerned.**—The units of electrical energy are the **coulomb**, which is the unit of quantity, and the **volt**, which is the unit of difference of potential (or pressure, so to speak). Faraday's law has to do only with the former. Equal numbers of coulombs liberate equivalent weights of all elements, but different voltages are required to decompose different compounds, according to their stability (see Chap. XXXVIII).

To liberate 1.008 g. of hydrogen, or one equivalent of any other element, 96,540 coulombs of electricity are needed. The charges on 1.008 g. of hydrogen ions must, therefore, equal this amount. There are  $6.07 \times 10^{23}$  molecules of hydrogen in 22.4 liters ( $\text{H}_2$ ) and therefore in 2.016 g. of the gas. A simple calculation shows therefore that each coulomb is distributed over about  $63 \times 10^{17}$  ions of hydrogen.

A current of 1 coulomb per second is called 1 **ampere**. Thus, the current passing through a 1-amp. lamp (or 2 half-ampere, 50

watt\* lamps in parallel) will liberate 1.008 g. (11.2 liters) of hydrogen in 96,540 seconds, or 26 hours and 49 minutes. The same current will liberate 107.88 g. of silver ( $\text{Ag}^+$ ), or 31.78 g. of copper ( $\text{Cu}^{II}/2$ ) from a cupric salt in the same time. A current of 5 amperes will accomplish the same result in one-fifth of the time.

In consequence of this, the liberation of hydrogen from a dilute acid by electrolysis, or the deposition of silver or copper, is used as a means of measuring quantities of electricity. The volume of hydrogen collected, or the increase in weight of the negative electrode in a cell, called under such circumstances a **voltameter** (measurer of coulombs, not volts), is a measure of the quantity of electricity which passes around the whole circuit of which it forms a part.

**Applications: Ionic Equilibrium.** — Since the ions are chemically different from their parent molecules, their formation represents a variety of chemical change. The change may not involve any chemical interaction with the water. It is simply a dissociation, i.e., reversible decomposition of the dissolved substance.

From the fact that the proportion of molecules ionized is shown to become greater as more and more of the solvent is added (p. 337), and that removal of the solvent diminishes the proportion of ions to molecules, and finally leaves the substance entirely restored to the molecular condition, we know that this is a reversible action and therefore a true dissociation. The molecules and their ions adjust themselves like the components in any case of chemical equilibrium (pp. 289–307):



These equilibria are all of precisely the same nature as that of phosphorus pentachloride vapor (p. 299), and the discussion of the latter should be reëxamined and applied by the reader. The sole difference is that here change in volume is effected, not by compression or by release of pressure, but by removing or adding water. **The adjustment to a condition of equilibrium, however, seems to be instantaneous where ions are concerned, while in other chemical actions it always takes a perceptible, and often a considerable interval of time. The chemical behavior of substances in ionic equilibrium will be discussed in the next chapter (see p. 377).**

\* No. amperes  $\times$  no. volts = no. watts. Hence, with 100 volts, a 50-watt lamp carries one-half ampere.

\* The mode of formulation previously used (p. 298) may be employed here. If  $[\text{NaCl}]$ ,  $[\text{Na}^+]$ , and  $[\text{Cl}^-]$  stand for the molecular concentrations (numbers of moles per liter) at equilibrium of the molecules, and the two ions, respectively, we have an equilibrium constant (*cf.* p. 298), in this case called the **ionization constant**:

$$K = \frac{[\text{Na}^+] \times [\text{Cl}^-]}{[\text{NaCl}]}$$

When we dissolve a single substance which gives only two ions, the molecular concentrations of the ions are necessarily equal. When some other ionogen with a common ion is present, however, the values of  $[\text{Na}^+]$  and  $[\text{Cl}^-]$  will be different.

**The Electrical Energy Required to Decompose Different Compounds.** — Chemical compounds are of very different degrees of stability, and hence the quantities of energy, electrical or otherwise, required to decompose them vary widely. Thus, hydrogen chloride is very stable, while hydrogen iodide is easily decomposed by heating. The disunion of one mole (equivalent quantities) of these substances in aqueous solution absorbs 39,300 cal. and 13,100 cal. of heat energy, respectively. Hence, although equal quantities of electricity (96,540 coulombs in each case) perform this office, very unequal amounts of electrical energy are used up in the electrolysis.

The energy in a stream of water is represented by the product of the quantity passing a given section and the pressure or head of water available at that point. If the pressure is low, the work that can be done will be small, even if the quantity flowing is great. So electrical energy is expressed by the product of the current strength, or quantity of electricity passing per second during a certain period of time, and the electromotive force. The latter corresponds to pressure, and is defined by the difference in potential of two points in the circuit between which the energy is being used up.

Now, in the series of cells which was described (p. 351), each cell, while being traversed by the same quantity of electricity as any of the others, cuts down the electromotive force of the current in proportion to the amount of energy consumed by the decomposition going on within it. Hence, while a voltmeter will show no difference in potential between two neighboring parts of the heavy wires used as connec-

\* The content of this paragraph is referred to in Chap. XX, but is not employed systematically until Chap. XXXIV is reached.

tions, for no work is being done in the wires, it will show a considerable difference in potential between two points which are separated by one of the cells.

A system of cars hauled by a cable is analogous to our set of cells and more familiar. When clutched to the cable, all the cars move with equal speed, but, being loaded with different numbers of passengers, take very different amounts of power from the moving cable.

We should infer from this, that to decompose every electrolyte, a current of a certain minimum electromotive force, sufficient to furnish the fall in potential necessitated by the chemical change, which would be different in different cases, would be required. This is found to be the case. For the easy decomposition of sulphuric acid and liberation of the products an electromotive force of at least 1.92 volts is necessary, for hydrochloric acid 1.41 volts, for hydriodic acid 0.53 volts, for zinc sulphate 2.7 volts, and for silver nitrate 0.70 volts. When we use a current of electromotive force falling short of that specified, we find that the flow of electricity is interrupted. The electrolytic cell practically forms a break in the circuit (see Chap. XXXVIII).

**Polarization.** — It is found that when plates of platinum, a metal which is not acted upon by the liberated radicals, are used, the products of electrolysis accumulate on the electrodes and tend to produce a reverse current (see Electromotive chemistry). The cell is said to be **polarized**. Thus, after hydrochloric acid has been electrolyzed for a few moments, hydrogen and chlorine adhering to the two platinum plates set up this current.\* If the battery is disconnected, the electrolytic cell becomes for a brief time itself a battery, the re-ionization of the hydrogen and chlorine (reproducing hydrochloric acid) furnishing the energy. It is the continuous overcoming of this reverse current, and prevention of the re-ionization, that demands the minimum electromotive force (here 1.41 volts) of which mention has just been made.

It is possible to arrange cells in which no polarization can take place. Thus, when we electrolyze cupric sulphate between *copper* electrodes, the copper is deposited upon one plate and the  $\text{SO}_4$  removes the copper from the other plate, forming cupric sulphate, thus restoring the electrolyte to its original condition. The only difference is that a portion of the copper has been deposited on one pole and an equivalent amount has been removed from the other (see Copper

\* If copper plates are used, cupric chloride is formed at the positive plate (anode), and no polarization can occur at that plate.

refining). With such cells, no minimum difference in potential is required to effect electrolysis, for there is no polarization current to be overcome. The feeblest electric current will produce continuous, if slow, chemical change.

This result is extremely interesting, for it shows that the operation of migration in itself does not require the consumption of much energy. If the molecules were actually torn apart by the electricity, then all electrolytic operations would require a minimum electromotive force for their maintenance. The fact just stated, therefore, is significant, for it confirms the present views in regard to the theory of solutions. This fact is in agreement with the belief that the actual production of the ions is accomplished by the water in advance, and quite independently of the use of electricity, and that the sole function of the electricity in the process of electrolysis *within the solution* consists in the pilotage of the ions in reverse directions according to their charges, an operation which necessarily consumes but little energy. The friction alone of the moving ions has to be overcome. It makes clear the fact that it is only when the chemical change in the cell involves the actual decomposition of some material, accompanied (as in the electrolysis of hydrochloric acid) by the final delivery of the constituents in the free state, that considerable consumption of electrical energy, proportional to the extent of the chemical change, must take place.

**Applications: The Conductivity of Electrolytes for Electricity.** — The facility with which equi-molar solutions of different substances conduct electricity, when they are placed under like conditions, depends jointly, (1) on the degree of ionization, (2) on the speed with which the ions move, and (3) on the valence of the ions.

This is easily explained. Equal numbers of the original molecules are used in making the different solutions being compared (equi-molar solutions). Evidently the greater the percentage of the molecules of the solute which is ionized (1), the larger the number of the ions present, and the greater the facilities for transporting electricity through the solution. Also, with equal numbers of ions, those which move fastest (2) will carry the most electricity through the solution. Finally, with equal numbers of ions, and equal speeds, ions with higher valence (3), and therefore more unit charges per ion, will carry more electricity than will ions with only one charge per ion (univalent ions). The case is like ferrying an army across a river. The number of soldiers passing per hour will depend, (1) upon the number of boats



available, (2) upon the speed with which each boat moves, and (3) upon the capacity of each boat.

When equivalent instead of equi-molar amounts are compared, the last of these factors, the valence, drops out of consideration.

The most highly dissociated acids, as we should expect, since they give large numbers of the speedy hydrogen ions, are the best conductors. The highly ionized bases, such as potassium and sodium hydroxides, come next. The best conductors among salts fall considerably behind both of these, because, although their degrees of ionization may not be less than those of the best conducting acids and bases, their ions all move more slowly than do hydrogen-ion and hydroxide-ion. On the other hand, concentrated solutions all conduct badly, relatively to the number of molecules originally used in making them, because only that proportion of the substance which is ionized contributes to the conduction (p. 358). All this is just what we should expect, in view of our hypothesis, for the passage of the electricity must be dependent upon the frequency with which discharges of the ions upon the electrodes occur, and this, in turn, must depend upon both the concentration and the speed of the ions. To return to an analogy used once before, the rate at which a fluid can be transferred between two reservoirs must depend upon the denseness of the array of buckets available, on the speed with which they are moved, and on their individual capacity.

Ordinarily, it is the resistance which a substance presents to the passage of the electric current which is measured. Obviously, however, for the present purpose it is more convenient to give expression to the reciprocal of this value, which we term the **conductivity**. In order that the results may have chemical significance, we express them in terms of the conducting power of one gram-equivalent of the compound dissolved in water and placed in a narrow cell whose opposite walls, of great area and situated one centimeter apart, form the electrodes. Since the water is a nonconductor, the conducting power of the solution intervening between the plates is a measure of the capacity of the dissolved substance for facilitating the discharge between the poles.

**Applications: To the Interpretation of Conductivity Measurements.** — We have seen that when the solution of an ionogen is diluted, the proportion of ions to undissociated molecules increases, while removal of a part of the solvent has the opposite effect (p. 358). Now, a change in the number of ions naturally

modifies the capacity of the liquid for carrying electricity, so that observation of the changes in the conductivity of a solution, when the concentration is altered, supplies the simplest means of studying the phenomena of ionization.

A glass trough and amperemeter \* (Fig. 106) may be used to illustrate this principle. The electrodes are long strips of copper foil, which pass down at the ends of the trough and are situated, not one centimeter, but ten or fifteen centimeters apart, in order that the

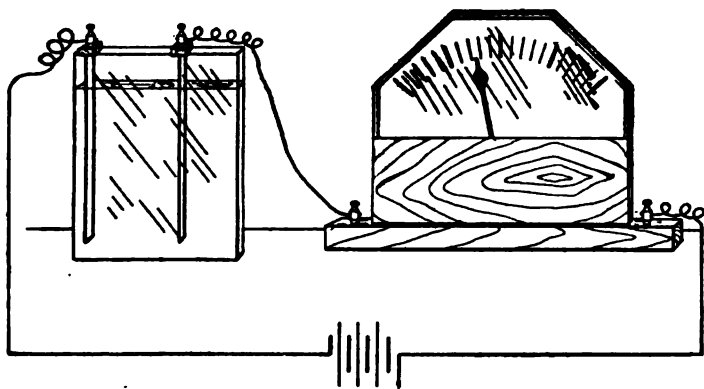


FIG. 106.

contents of the vessel may be more easily seen. After placing the two instruments in circuit with a source of electricity, we first pour very pure water into the cell. With this arrangement, the amperemeter does not indicate the passage of any current of electricity. Concentrated (36 per cent) hydrochloric acid is next cautiously added through a long-stemmed dropping funnel, so that it forms a shallow layer below the water. The situation at this stage is that a definite amount of hydrogen chloride dissolved in a *small* amount of water fills what was before a nonconducting gap in the electric circuit. The deflection of the needle in the amperemeter indicates that a certain current of electricity is able to pass through this acid. When we now stir the surface of the acid very gently with a thin glass rod, the amperemeter instantly responds, showing an increase in conductivity. As we stir, the conductivity increases, and the increase ceases only when the liquid has become homogeneous. Introduction of an

\* For these experiments an amperemeter of low resistance, 0.5–1 ohm, must be used, and a battery of one or two accumulator cells is sufficient.

additional supply of water will improve the conductivity still more, but the effect becomes less and less, until no change on further dilution is perceptible. Reasoning about these effects, we perceive that the *amount* of hydrochloric acid has not altered during the experiment. Yet the quantity of conducting material between the electrodes must have become greater, for the carrying power of the whole has improved. We were therefore observing the progress of a chemical change of the nonconducting hydrogen chloride into conducting materials. Hydrogen chloride molecules do not carry electricity (p. 211), but the hydrogen and the chloride ions, into which they were gradually altered by chemical change during the stirring, do carry electricity. Furthermore, the change practically ceased at great dilution, for the dissociation into ions was then practically complete. If we could conveniently have started with only liquefied, dry hydrogen chloride in the cell, we should have observed the whole range of changes from zero to the maximum.

When a saturated solution of cupric chloride is used instead of the hydrochloric acid, dilution is accompanied by a similar improvement in conductivity. Here we notice, besides, that the yellowish-green liquid with which we start changes to a pale blue, as the molecules of cupric chloride are dissociated and the color of the solution becomes more exclusively that of the copper ions. When the solution has become perfectly blue, further dilution is seen to affect the conductivity but slightly.

The approach to a maximum of conductivity reached in these two cases indicates that practically the whole of the material has assumed the ionic form. Theoretically the absolute maximum would be reached at infinite dilution. The conductivity of the same amount of substance in more limited dilution is that of the proportion of ions corresponding to this dilution, since the complete molecules, still present, are without influence on conductivity. Thus the ratio of the conductivity at a given dilution to the maximum conductivity is equal to the proportion of the whole material ionized at the given dilution. From a series of measurements for a fixed amount of a substance at different dilutions, after the results have been plotted, we can usually (see, however, below) ascertain the limiting, maximum conductivity by graphic extrapolation. If  $\lambda_v$  is the conductivity of an equivalent of the substance dissolved in  $v$  liters of water, and  $\lambda_\infty$  the conductivity of the same amount at infinite dilution, then  $\lambda_v/\lambda_\infty$  is the proportion of molecules completely ionized in the former solution.  $\lambda_v$  is called the **equivalent conductivity** at the dilution  $v$ .

The following numbers show the equivalent conductivities at 18° of solutions of four different substances, expressed in the units always employed for the purpose (which are reciprocal ohms). The symbols  $\lambda_{0.1}$ , meaning 1 equivalent in 0.1 l.;  $\lambda_1$ , meaning 1 equivalent in 1 l.; and so forth, denote the concentrations.

	$\lambda_{0.1}$	$\lambda_1$	$\lambda_{10}$	$\lambda_{100}$	$\lambda_{\infty}$ (Calc.)
Hydrochloric acid . . . .	64.4	301.0	351.0	370.0	384
Sodium chloride . . . . .	.....	74.4	92.5	103.0	110
Sodium acetate . . . . .	.....	41.2	61.1	70.2	78
Acetic acid . . . . .	0.05	1.32	4.6	14.3	(352)

It will be seen from inspection of these figures that in the case of the first three substances, the conductivity does not improve much when a solution containing one equivalent in 10 l. is diluted ten times, and that further dilutions, no matter how extensive, produce a still smaller effect. The case of acetic acid requires separate consideration (see next section).

Thus, measurements of conductivity enable us to study the ionic decomposition of all ionogens, and to state accurately the fraction ionized, at each concentration, in solutions of every ionogen. This information is obviously most valuable, for it places us in a position to know the exact constitution of every solution we use in the laboratory. In the next section but one the data on which such knowledge can be based is given. In the following chapter the mode of applying the data is explained.

**The Case of a Little-Ionized Substance.** — Acetic acid, a feebly ionized substance, as the table shows, conducts very badly in concentrated solution and, while the conductivity improves with dilution, it is not possible experimentally to observe any approach to the maximum conductivity. The conductivity, in cases like this, is still far removed from the maximum at dilutions at which, with other substances, the maximum is nearly attained.

In cases like that of acetic acid, the conductivity at infinite dilution cannot be estimated by extrapolation. But fortunately another method is available. The values 384, 110, and 78 for  $\lambda_{\infty}$  in the cases of the first three substances can be reached by extrapolation, and represent the conducting powers of equal numbers of ions, for there are equal numbers of equivalents present and no molecules remain un-ion-

ized. These values are unequal solely because of the differing speeds of the ions concerned. Each of them derives its value from numbers representing the relative speeds of the two ions present, and must be the sum of these two numbers. If, therefore, we measure the relative speeds of the two ions (p. 347) of one of the substances, we can divide the value of  $\lambda_{\infty}$  in this proportion and learn the part which each ion contributes to the total. Dividing 384 in this way we get the speed of  $\text{H}^+ = 318$  and of  $\text{Cl}^- = 65.9$  already given (p. 347). Dividing  $\lambda_{\infty}$  for sodium acetate (78), similarly, we get the speeds  $\text{Na}^+ = 44.4$  and  $\text{CO}_2\text{CH}_3^- = 33.7$ . The speeds of  $\text{Cl}^-$  and  $\text{Na}^+$  together ( $65.9 + 44.4 = 110.3$ ) must then equal  $\lambda_{\infty}$  for  $\text{NaCl}$  and, as we see, they do. Similarly, the speeds of  $\text{H}^+$  and  $\text{CO}_2\text{CH}_3^-$  together ( $318 + 33.7 = 351.7$ ) must equal  $\lambda_{\infty}$  for  $\text{HCO}_2\text{CH}_3$ , although we cannot observe the latter directly. This method can be applied to all of the less highly ionized acids and bases, for their sodium and potassium salts belong invariably to the class of substances which are most ionized, and for which, therefore,  $\lambda_{\infty}$  can be determined accurately by extrapolation.

***Composition of Solutions of Ionogens: Fractions Ionized.***

— The rule, degree of ionization  $= \lambda_s/\lambda_{\infty}$  (p. 364), enables us to calculate the value for any dilution, when the necessary data are given. We need only the values of the conductivity ( $\lambda_s$ ) for different dilutions (p. 365) and those of the relative speeds of each kind of ions expressed in the same units. The latter, when added, give  $\lambda_{\infty}$ .

Thus, hydrogen chloride in a solution containing 1 equivalent in 0.1 l. (365 g. per liter), which would be a rather concentrated hydrochloric acid, shows the fraction ionized  $\frac{64.4}{384}$ , or 0.168 (= 16.8 per cent). Normal hydrochloric acid is ionized to the extent of  $\frac{301}{384}$ , or 0.784; normal sodium chloride,  $\frac{74.4}{110}$ , or 0.676; normal acetic acid,  $\frac{1.32}{352}$ , 0.004 (= 0.4 per cent).

The **dilute acids** used in the laboratory are generally of six times normal (6N) concentration. But, often, we add only a drop or two to a large bulk of liquid, so that the acids are commonly very dilute as actually employed. The **solutions of salts** are of different strengths, but the great majority are of normal (N), or even smaller concentrations. In practice they, also, are still further considerably diluted before use. If, therefore, we give the **fractions ionized** (total molecules of ionogen = 1) in **decinormal solutions** (except where otherwise specified), the reader will be able to estimate roughly the proportion of each kind of ions in any application of the reagent.

In the case of acids containing more than one displaceable hydrogen unit, the kind of ionization on which the figure is based is indicated by a period. Thus  $\text{H.HCO}_3$  means that the whole of the ionization is assumed to be into  $\text{H}^+$  and  $\text{HCO}_3^-$ .

## FRACTION IONIZED IN 0.1N SOLUTIONS AT 18°

## ACIDS

Nitric acid . . . . .	0.92	Carbonic acid (N/25) . . . .	0.0021
Nitric acid (conc., 62%) . . .	0.09	Hydrogen sulphide, $\text{H.HS}$ . .	0.0007
Hydrochloric acid . . . . .	0.92	Boric acid, $\text{H.H}_3\text{BO}_3$ . . . .	0.0001
Hydrochloric acid (conc., 35%)	0.13	Hydrocyanic acid . . . . .	0.0001
Sulphuric acid, $\text{H.H}_2\text{SO}_4$ . . .	0.61	Permanganic acid (N/2) . . .	0.93
Sulphuric acid (conc., 95%) . .	0.01	Hydriodic acid (N/2) . . . .	0.90
Hydrofluoric acid . . . . .	0.15	Hydrobromic acid (N/2) . . .	0.90
Oxalic acid, $\text{H.HC}_2\text{O}_4$ . . . .	0.50	Perchloric acid (N/2) . . . .	0.88
Tartaric acid, $\text{H.HT}$ . . . . .	0.08	Chloric acid (N/2) . . . . .	0.88
Acetic acid (N) . . . . .	0.004	Hypochlorous acid . . . . .	0.0002
Acetic acid . . . . .	0.013	Phosphoric acid, $\text{H.H}_3\text{PO}_4$ . .	0.27
Carbonic acid, $\text{H.HCO}_3$ . . . .	0.0017	<b>Water</b> . . . . .	0.041

## BASES

Potassium hydroxide . . . . .	0.91	Aminonium hydroxide . . . . .	0.013
Sodium hydroxide . . . . .	0.91	Strontium hydroxide (N/64) . .	0.93
Barium hydroxide . . . . .	0.77	Barium hydroxide (N/64) . . .	0.92
Lithium hydroxide (N) . . . . .	0.63	Calcium hydroxide (N/64) . . .	0.90
Tetramethylammonium hy-		Silver hydroxide (N/1783) . . .	0.39
dride (N/16) . . . . .	0.96	<b>Water</b> . . . . .	0.041

## SALTS

Potassium chloride . . . . .	0.86	Sodium bicarbonate,	
Potassium nitrate . . . . .	0.83	$\text{Na.HCO}_3$ . . . . .	0.78
Potassium acetate . . . . .	0.83	Sodium phosphate, $\text{Na}_2\text{HPO}_4$	0.73
Potassium sulphate . . . . .	0.72	Sodium tartrate . . . . .	0.69
Potassium carbonate . . . . .	(0.71)	Barium chloride . . . . .	0.77
Potassium chlorate . . . . .	0.83	Calcium sulphate (N/100) . . .	0.64
Ammonium chloride . . . . .	0.85	Cupric sulphate . . . . .	0.39
Sodium chloride (N) . . . . .	0.66	Silver nitrate . . . . .	0.81
Sodium chloride (N/2) . . . . .	0.74	Zinc sulphate . . . . .	0.40
Sodium chloride . . . . .	0.84	Zinc chloride . . . . .	0.73
Sodium nitrate . . . . .	0.83	Mercuric chloride . . . . .	(<0.01)
Sodium acetate . . . . .	0.79	Mercuric cyanide . . . . .	Minute
Sodium sulphate . . . . .	0.70		

In addition to their use in showing the nature of the reagents employed in the laboratory (p. 365), these numbers show also to what extent any pair of ionic substances will unite when mixed (see pp. 377, 380-382), and they likewise indicate the chemical activity of the ionogens when in solution (see next section).

Misapprehension easily arises in regard to the inferences that may be drawn from a conductivity value. A single such value, say that for salt at 10 l. dilution (92.5), gives no information about the extent of ionization. We must have the value at infinite dilution as well, that is, we must have the other term of the ratio corresponding to complete ionization, before the proportion of the molecules ionized at the 10 l. dilution can be known. Further, we must have the values of both for the same salt, at the same temperature and in the same solvent, for the values at all dilutions change markedly when any one of these conditions is altered. Thus the conductivity of normal sodium chloride solution at 50° is 120, and is therefore actually greater than at 18° when the dilution is infinite. But at 50° the conductivity at infinite dilution is 185, so that at this temperature the degree of ionization is  $\frac{120}{185}$  or 0.65, about the same as at 18°. On the other hand, when a little alcohol is added to the aqueous solution, the conductivities all diminish. But that at infinite dilution diminishes also, so that the proportion of the material ionized does not seem to be greatly affected. The chief effect of raising the temperature is simply to diminish the friction opposing the motion of the ions and, therefore, to increase the conductivity. The change is about 2 per cent for each degree. Addition of alcohol, on the other hand, increases the friction and diminishes the conductivity. There is, however, a real, though usually smaller, change in the degree of ionization with change in temperature. When the temperature is raised, the fraction ionized increases or diminishes according as the heat of ionization is negative or positive (cf. p. 305), and conversely when the temperature is lowered.

**Degree of Ionization of Water.** — If we consider a liter of water as a normal solution in which 18 g. (one mole) represents the solute and the rest stands for the solvent, the conductivity for complete ionization into  $H^+$  and  $OH^-$  would be  $318 + 174 = 492$ . The actual ionization is one ten-millionth part of this. In other words, there is only one ten-millionth of 1 g. of hydrogen-ion and the same fraction of 17 g. of hydroxide-ion in a liter of water. A column of water 1 cm. long (18°) conducts less well than a column of mercury of equal cross-section and over 1,700,000 miles in length.

With some substances, as the temperature is continuously raised, the fraction ionized increases to a maximum and then diminishes. With water, the maximum is reached at 229° (Arrhenius) or 250-275° (A. A. Noyes). Ammonium hydroxide and acetic acid also exhibit

similar maxima. In these cases, the heat of ionization changes its sign, being at first negative, and, beyond the maximum, positive (cf. p. 305).

**Relation of Ionization to Chemical Activity.** — These tables may be used for reference. The import of the following general statements, drawn from the tables, *should be memorized*:

1. **Salts**, with the exception of those of mercury, are all well ionized. In actions involving their ions, salts are therefore **all of the same order of activity**, for a dilute solution of every salt contains a large amount of the ionic components.

Occasionally, the differences in the degrees of ionization of salts have to be considered. The rule is simple. Salts with two univalent radicals are the most highly ionized (*e.g.*,  $\text{KCl}$  86 per cent,  $\text{KNO}_3$  83 per cent). Those with one bivalent radical are less ionized (*e.g.*,  $\text{K}_2\text{SO}_4$  72 per cent,  $\text{K}_2\text{CO}_3$  71 per cent). Those with two bivalent radicals are still less ionized (*e.g.*,  $\text{CuSO}_4$  39 per cent,  $\text{ZnSO}_4$  40 per cent). Those containing one trivalent radical are less ionized than are those with one bivalent radical.

2. **Acids** show the most extreme differences in their degrees of ionization. That is to say their solutions must contain very different concentrations of hydrogen-ion. Since their activity as acids depends on this substance (p. 340), and the activity of a substance is proportional to its concentration (p. 292), it follows that **acids will show very great differences in apparent chemical activity**. At this point, therefore, we emerge from semi-physical discussion of the subject and reach something of definite, practical application in chemical work.

The data show that acids may be divided roughly into four classes with different degrees of acidic activity:

(a) The ionization in decinormal solution exceeds 70 per cent; *e.g.*, nitric acid and hydrochloric acid. These are the acids which are chemically most active, for their solutions contain relatively high concentrations of hydrogen-ion.

(b) The ionization is between 70 and 10 per cent; *e.g.*, sulphuric acid and phosphoric acid. These acids are noticeably less active, for their solutions contain lower concentrations of hydrogen-ion.

(c) The ionization is between 10 and 1 per cent; *e.g.*, acetic acid. These are the weaker acids, for their solutions contain very small concentrations of hydrogen-ion.

(d) The ionization is less than 1 per cent; *e.g.*, carbonic and



boric acids. These are the feeble acids, for their solutions contain only minute concentrations of hydrogen-ion.

3. The **bases** show two classes:

(a) Ionization high; *e.g.*, potassium hydroxide. These bases are active, for their solutions contain high concentrations of hydroxide-ion.

(b) Ionization less than 2 per cent; *e.g.*, ammonium hydroxide. These bases are weak on account of the low concentration of hydroxide-ion.

4. **Water** is less ionized than any other substance in the list. It shows therefore, as we already know, usually little or no interaction with acids, bases, or salts, and hence is valuable as a solvent for these substances. Its ions are  $H^+$  and  $OH^-$ , and it is thus as much an acid as a base.

**Exercises.** — 1. With solutions of the following substances, state, (a) what will be the products of electrolysis, (b) whether each is primary or secondary, and (c) how they may be isolated in each case: Potassium chlorate, potassium iodide, potassium iodate, silver sulphate, sodium peroxide, sodium fluoride.

2. Make equations (p. 358) showing the ionic and molecular materials in solutions of potassium bromide, potassium bromate, sodium periodate, aluminium chloride, zinc sulphate. Mark the charges on the ions and give the name of each ionic substance (p. 356).

3. Prepare lists of other anions and cations which have been encountered, giving the formula and number of charges of electricity in each case.

4. How many coulombs are carried by or will deposit: 20 g. of silver, 15 g. of antimony, 30 g. of chlorine, 60 g. phosphate-ion ( $PO_4$ )?

5. What current strength (in amperes) is required to deposit: 20 g. of silver in an hour, 100 g. of iodine in 5 minutes, 60 g. of antimony in 3 hours?

6. What is the percentage of molecules ionized in: deci-normal ( $N/10$ ) sodium chloride, centi-normal ( $N/100$ ) acetic acid, centi-normal hydrochloric acid (p. 365)?

7. If 1 c.c. of dilute hydrochloric acid (6*N*) is added to 30 c.c. of an aqueous solution, what is the reacting concentration of the acid?

8. Classify all the acids in the table (p. 367) according to the four classes (p. 369).

9. Two troughs, one 4 inches long and the other a mile long, are

**filled with cupric sulphate solution, and a plate of copper with a wire connection is inserted at each end of each trough. The pairs of plates are connected *simultaneously* with a battery or dynamo. If there is any difference, in which cell will the deposit of copper on the electrode appear first, and about how long will be the time required for its appearance in the other cell?**

## CHAPTER XIX

### IONIC SUBSTANCES AND THEIR INTERACTIONS

BEFORE considering the typical interactions of ionogens in solution, we must have a clear conception of the peculiarities of these bodies which are likely to affect their behavior. The facts on which such a conception must be based have been given in preceding chapters, and all that is now necessary is to collect and apply these facts.

In this discussion, after enumerating the various kinds of ionic substances, it must be made clear that aqueous solutions of ionogens are mixtures containing several solutes. We then consider the relations of the ionic and the molecular substances, in equilibrium, when a single ionogen is present. It must also be shown that each kind of ions is a distinct substance with individual physical and chemical properties. Next, salts being used for illustration, the commonest kind of interaction, double decomposition between ionogens, will be discussed. In this connection precipitation brings up the peculiar state of equilibrium between the undissolved solute and the complex of molecules and ions in solution. The interaction of acids and bases (neutralization) then follows. Weak acids and bases and hydrolysis of salts are next discussed. Finally, the five varieties of ionic chemical change are given, and the practical importance of actions in which ions play no part is emphasized.

The discussion of systems in equilibrium in the present chapter will be almost purely qualitative. The quantitative consideration of ionic equilibria (*cf.* p. 359) is postponed until the study of the metals and their compounds is taken up (see Chap. XXXIV).

*The Classes of Ionogens.* — Acids are classified according to the number of replaceable hydrogen units in their molecules. Thus chloric acid  $\text{HClO}_3$  is a monobasic acid, sulphuric acid  $\text{H}_2\text{SO}_4$ , a dibasic acid and phosphoric acid  $\text{H}_3\text{PO}_4$  a tribasic acid. These terms relate to the fact that, in neutralization (see p. 386) the acids interact with one, two, or three molecules of a base like sodium hydroxide.

**Bases** are named in a similar way: sodium hydroxide  $\text{NaOH}$  is a **monoacid base**, calcium hydroxide  $\text{Ca(OH)}_2$  is a **diacid base**.

**Salts** like  $\text{KCl}$  and  $\text{Na}_2\text{CO}_3$  are **neutral** (see acid salts, below) or **normal salts**, and  $\text{NaKCO}_3$  and  $\text{Ca(OCl)Cl}$  (bleaching powder) are **mixed salts**.

The most interesting classes of mixed salts are the **acid salts** (p. 215) and the **basic salts**. In acid salts, like  $\text{NaHSO}_4$  (p. 206) and  $\text{NaH}_2\text{PO}_4$  (p. 207), all the hydrogen of the acid has not been replaced by a metal. In basic salts, like  $\text{Ca(OH)Cl}$ , part of the basic hydroxyl remains.

All these substances are ionogens (p. 355). The mixed salts are, naturally, dissociated into more than two ionic substances. For a fuller discussion of these and other salts see pp. 400-402.

**Ionic Substances Furnished by Acids.** — The mode of naming ionic substances has already been given (p. 356).

**Acids**, e.g.,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , when dissolved in water, all furnish hydrogen-ion  $\text{H}^+$  and a negative ionic substance (anion), e.g.,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ . The solutions differ from those of salts in the constant presence of hydrogen-ion, and in the absence of any other positive ion.

**Hydrogen-ion**  $\text{H}^+$  is a colorless substance. It is sour in taste, and its presence is recognized by the fact that it turns blue litmus red (see Indicators, p. 391). These properties serve as **tests** for acids, as they are not commonly interfered with by other substances which may be present. Hydrogen-ion is univalent and, when combined with negative radicals of salts, gives the (molecular) acids. The activity of acids depends upon the concentration of the hydrogen-ion they furnish (p. 369), and therefore upon their solubility and the degree of ionization of the dissolved molecules. Some furnish so little hydrogen-ion that their action on litmus can hardly be detected.

The substances of the composition  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and so forth, are commonly called acids. But it is only when they have been dissolved in water, or some other ionizing solvent, that they show the properties characteristic of acids. In fact, there is **only one acid**, hydrogen-ion  $\text{H}^+$ , although the substances which give it by dissociation are many. The parent substances are **salts of hydrogen**, in which the element hydrogen plays the part of a metallic element.

**Ionic Substances Furnished by Bases.** — **Bases**, e.g.,  $\text{KOH}$ ,  $\text{NH}_4\text{OH}$ ,  $\text{Zn(OH)}_2$ , all furnish hydroxide-ion  $\text{OH}^-$  and some positive

ionic substance (cation),  $K^+$ ,  $NH_4^+$ ,  $Zn^{++}$ . Their solutions differ from those of salts in the constant presence of hydroxide-ion and in the absence of any other anion. The more active bases, that is, those which are soluble and highly dissociated, so that they give a high concentration of hydroxide-ion, are called **alkalies**. Such are potassium and sodium hydroxides. They are often named caustic alkalies and, individually, caustic potash and caustic soda. The solutions are called lyes.

**Hydroxide-ion**  $OH^-$  is a colorless substance. Properties which serve as **tests** for bases are that hydroxide-ion possesses a soapy taste and turns red litmus blue (see Indicators, p. 391). It is univalent, and combines with positive radicals to form (molecular) bases.

The common bases, with the exception of the hydroxides of potassium, sodium, barium, strontium, calcium, and ammonium, are but slightly soluble in water. Hence, zinc hydroxide, for example, although it dissolves sufficiently to enable chemical action to take place slowly, does not give enough hydroxide-ion at one time to affect litmus paper. Magnesium hydroxide and lead hydroxide turn red litmus paper blue with difficulty. Doubtless the few molecules that do dissolve are almost all ionized:



but all the dissolved materials put together (0.01 g. per l.) will scarcely be weighable unless a considerable volume of the solution is evaporated.

Substances like potassium hydroxide, ammonium hydroxide  $NH_4OH$ , and zinc hydroxide  $Zn(OH)_2$ , are commonly called bases. But it is only in their aqueous solutions that the basic properties appear. There is **only one base**, namely, **hydroxide-ion**  $OH^-$ , and these substances are simply the source of it. The parent substances are salts of some metallic element, or group playing the part of a metallic element (*e.g.*,  $NH_4$ ), in which hydroxyl is the negative radical.

The name "base" was originally applied to the non-volatile, and therefore seemingly more fundamental part of a salt that remained behind when the salt was heated. Usually the negative radical is disintegrated, as in heating calcium carbonate:  $CaCO_3 \rightarrow CaO + CO_2 \uparrow$ . But, as a matter of fact, it is generally the oxide and not the hydroxide of the metal that remains. Still, the oxide, formerly named the base, often readily gives the hydroxide (*cf.* p. 149) to which the term "base" is now applied, and behaves similarly to it in many interactions (*cf.* p. 213).

**Ionic Substances Furnished by Salts.** — Salts furnish positive and negative ionic substances, which may be either simple or composite,  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ . Some ionic substances are colored,  $\text{Cu}^{++}$  (cupric-ion) blue,  $\text{Cr}^{+++}$  reddish-violet,  $\text{Co}^{++}$  pink,  $\text{MnO}_4^-$  (permanganate-ion) purple,  $\text{Cr}_2\text{O}_7^-$  (dichromate-ion) orange, but most of them are colorless,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Zn}^{++}$ ,  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^-$ . They vary in taste, some being salt, some astringent, some bitter. They carry electricity, but relatively less well than do hydrogen-ion and hydroxide-ion, on account of their slower migration. The ionic materials characteristic of salts do not effect litmus, and individual tests are required for each. Usually we add some other ionic substance, with which the ion thought to be present combines to form an insoluble, molecular substance of known color, or appearance, and examine the precipitate if any appears. Thus, when the presence of chloride-ion  $\text{Cl}^-$  is suspected, we may add a solution containing silver-ion  $\text{Ag}^+$ , expecting to obtain a precipitate of silver chloride  $\text{AgCl}$  ( $\text{Cl}^- + \text{Ag}^+ \rightarrow \text{AgCl} \downarrow$ ). In dilute solutions of salts, the ions are almost *always* numerous in comparison with the molecules (p. 369), so that salts are practically all active and their solutions almost always respond readily to the tests for the ions they contain. The art of detecting the various ionic substances present in a solution constitutes a large part of the branch of chemistry called qualitative analysis (see below).

All the known ionic substances are found in solutions of salts. The only ions which are not characteristic of salts, although sometimes occurring in their solutions (see acid and basic salts, above), are hydrogen-ion  $\text{H}^+$ , and hydroxide-ion  $\text{OH}^-$ .

It will assist the reader if the following facts are kept in mind. The elements which can form a simple positive ion are the **metallic** elements (p. 214, and see Chaps. XXII and XXXII). **Non-metallic** elements, like nitrogen, may be present in a positive ion, as in  $\text{NH}_4^+$ , but never exclusively. In other words, we know no such substances as nitrogen sulphate, or carbon nitrate. Conversely, the metals are frequently found in the negative ion, but never constitute it exclusively. They are then usually associated with oxygen, as in  $\text{MnO}_4^-$ , and  $\text{Cr}_2\text{O}_7^-$ .

**Solutions of Ionogens are Mixtures, in which Each Kind of Ion Acts Independently.** — We are accustomed to regard a bottle of sodium chloride solution as containing but one thing, aside from the water. We must now think of it as containing at least three

dissolved substances, any one of which might be alone responsible for some property of the solution. The same idea must accompany our use of every solution of an ionogen.

Numberless facts show that each kind of ion, for example cupric-ion, has an individual set of physical and chemical properties and behaves in many ways as if alone present in the solution. We shall meet with much evidence of this in the sequel. Some facts tending to prove it, that have already been given, may be recalled (*cf.* p. 339).

If, in comparing the migration speeds of any element, say copper, in different salts (p. 345), they were the motions of substances like  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{CuBr}_2$ ,  $\text{CuSO}_4$ , that we were comparing, all analogy teaches us that the speeds with which they would move should vary widely. That the blue color drifts always at the same pace shows that it is the same substance, namely cupric-ion  $\text{Cu}^{++}$ , that we are observing.

If, in solutions of the different permanganates,  $\text{KMnO}_4$ ,  $\text{NaMnO}_4$ ,  $\text{Ba}(\text{MnO}_4)_2$ , and so forth, the dissolved bodies were different in each case, we should confidently expect the purple colors of the solutions to differ markedly in shade. But, for dilute solutions of equivalent concentrations, when strict examination is made, the tints are found to be absolutely identical. We are therefore simply comparing different mixtures all containing the same proportion of the same free, colored body,  $\text{MnO}_4^-$ .

In phosphorus pentachloride vapor (p. 260), the fully liberated trichloride and chlorine are prominent components. Diminishing the volume of a fixed amount of this mixture, by compression, throws more chlorine into combination and the total absorption of blue light (from which the greenish-yellow color is derived) becomes less, the compounds of phosphorus being both colorless. Increasing the volume, on the other hand, promotes the dissociation and increases the depth of the yellow color. The system of ions and molecules in equilibrium in a solution of cupric bromide (see below), or any other ionogen, behaves in exactly the same way. The components possess and exhibit individual properties, much like the components of a gaseous mixture (p. 111), both in this and in other respects.

All solutions of acids are sour in taste, irrespective of the nature of the negative ion, while salts containing the same negative radical are not sour at all. Hence in solutions of acids we are tasting the same free substance, hydrogen-ion  $\text{H}^+$ . Similarly, in solutions of all alkalies, we note the soapy taste of hydroxide-ion  $\text{OH}^-$ .

These illustrations concern physical properties. In the later sections we shall learn that an ionic material, such as bromide-ion

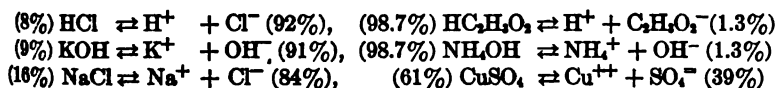
or cupric-ion, has specific *chemical* properties irrespective of the nature of its concomitants.

### IONIC EQUILIBRIUM

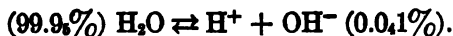
**The Ionic Equilibrium Involving a Single Ionogen.**— In the ionization of a molecular substance, the chemical change is incomplete and the system reaches a condition of equilibrium (p. 358). The action is, therefore, reversible, and there are thus **two routes** to the **same equilibrium point**. This fact must not be forgotten, for we have to consider the union of ionic substances even more often than the converse change. Now, the **degrees of ionization** of various ionogens tell us the location of the equilibrium point, and therefore the **extent of the chemical change** involved in reaching this point by **either route**, that is, either by the dissociation of molecules or by the union of ions. In a class of interactions, of which all are incomplete, and only those are interesting and useful which approach completeness, we require some means of knowing which are complete and why they are so. The table of fractions ionized (p. 367) supplies most of the required information.

To illustrate, take the case of a single ionogen. When we place hydrogen chloride in decinormal solution, 0.92 of the molecules dissociate. Conversely, when we start with the hydrogen-ion and chloride-ion, say by mixing two solutions, each of which contains **one of them** (along with another ion), then  $1 - 0.92$ , or only 0.08 (= 8 per cent) of these ionic substances will combine.

This exemplifies the case of an active acid. The following equations show the data for six typical substances in *N/10* solution, namely, two acids, two bases, and two salts:



These samples are chosen to illustrate, in each pair, the extremes. Thus, when potassium-ion and hydroxide-ion are brought together little union takes place, while with ammonium-ion and hydroxide-ion the union is practically complete. In the case of the soluble **salts**, however, there are almost (p. 369) no cases of considerable union of the ions in dilute solutions. The case of water, on the other hand, is one of the most extreme:



Hydroxide-ion and hydrogen-ion thus unite almost completely.



Similar reasoning enables us to handle the more complex, but very common case of the mixing of two ionogens. The degrees of ionization tell us the exact condition of each system separately, before mixing. The result of the mixing is best understood by viewing the change as consisting in a *displacement* of each of the equilibria by the action of the components of the other. We consider, therefore, next, the displacement of ionic equilibria.

**The Displacement of Ionic Equilibria.** — Equilibria are displaced by changes which favor or disfavor one of the opposed actions (p. 290). There may be either, (1) a physical change in the conditions, or a chemical interaction which (2) increases the amount of, or (3) removes one of the interacting substances. Each of these may be illustrated in turn.

1. As an example of the first, we have the effect of changing the amount of the solvent (p. 337). Adding more of the solvent reduces the concentration of the ionic materials and disfavors their union, so that it indirectly promotes dissociation. The larger the volume in which the ions are scattered, the less often will they meet, and the smaller the amount of combination. On the other hand, evaporating off a part of the solvent favors the encounters of the ions and promotes combination. When the solvent is at last entirely gone, the whole material is molecular.

In cases where the ionic and molecular substances are all colorless, these changes can be followed only by a study of the freezing-points or other similar properties of the solutions (p. 336). But when the substances are of different colors, the changes can also be seen. Thus, cupric bromide in the solid form is a jet black, shining, crystalline substance. When treated with a small amount of water it forms a solution which is of a deep reddish-brown tint, giving no hint of resemblance to a solution of any cupric salt. This doubtless represents the color of the molecules. When more water is added, the deep brown gives place gradually to green, and finally to blue. The latter is the color of the cupric-ion  $\text{Cu}^{++}$ , and is familiar in all solutions of cupric salts. The colorless nature of solutions of potassium and sodium bromides shows that bromide-ion  $\text{Br}^-$  is without color. Hence, in the present instance it is invisible. We are thus watching the forward displacement of the equilibrium:



If 1 g. of the solid is taken, it dissolves in about its own weight of

water, and independent measurement shows that there is relatively little ionization. Hence the solution is deep brown. When 10 c.c. of water has been added, 70 per cent of the salt is ionized, and the solution is green. With 40 c.c. of water, only 19 per cent remains in molecular form, and the blue color of the cupric-ion entirely overbears the tint of the molecules. If we now remove the water by evaporation, all these changes are reversed. When 30 c.c. of the water has been driven off, the solution is green. As the evaporation of the remaining 10 c.c. progresses, the brown color appears. When the water is all gone, the black residue remains. Here we are observing the backward displacement of the equilibrium,  $\text{CuBr}_2 \rightleftharpoons \text{Cu}^{++} + 2\text{Br}^-$ .

2. Cupric bromide may be used to illustrate also the chemical methods of displacing equilibria. Thus, we may show the **effect of adding more of one of the reacting substances**. If, at the green stage, we dissolve solid potassium bromide in the liquid ( $\text{KBr} \rightleftharpoons \text{K}^+ + \text{Br}^-$ ), the increased concentration of bromide-ion causes more extensive interaction of the ions, and the molecules, with their brown color, become prominent again. Adding cupric chloride increases the concentration of cupric-ion and has the same effect. In either case, renewed dilution with water reduces the concentrations of all the ions once more, the molecules become fewer, and the brown color is displaced by the blue for the second time.

3. Finally, the displacement of the same equilibrium by **removing one of the interacting substances** may be illustrated. Thus, if the chocolate-brown solution, in which molecular cupric bromide predominates, is shaken with pulverized lead nitrate (and filtered), two changes are noticed. A pale yellow precipitate of lead bromide appears ( $\text{Pb}^{++} + 2\text{Br}^- \rightarrow \text{PbBr}_2 \downarrow$ ), and the *brown color fades into green*. Here the displacement is the opposite of the last. Instead of reinforcing one of the ions, we have reduced the concentration, and in fact almost entirely removed one of them, namely  $\text{Br}^-$ . This has, naturally, stopped the interaction of the  $\text{Cu}^{++}$  and  $\text{Br}^-$  which reproduces the brown, molecular  $\text{CuBr}_2$ . Hence the dissociation of the latter has continued to exhaustion of the whole molecular material.

The reader will find that the behavior of these ionic equilibria; and the way in which we discuss and explain it, are complete parallels of the behavior and explanation in the case of ordinary equilibria (pp. 169, 301), which should now be reexamined. The illustrations in the present section, and particularly the third (*cf.* p. 208), should

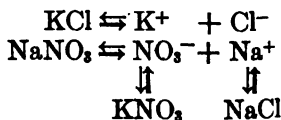
be considered until every feature is perfectly clear. They furnish the key to understanding the applications which follow. **One fact must not escape notice**, and that is that in none of the three instances was the forward action (the dissociation) in itself affected. The molecules of cupric bromide have, as we should expect, a certain tendency to decompose. No encounters between these molecules are required for mere decomposition. Hence their decomposition is not influenced by their nearness to, or remoteness from one another (illustration 1), nor by the presence of any other kinds of molecules or ions (illustrations 2 and 3). The effect, whether it involved an apparent increase, or a diminution of the dissociation, *was always accomplished by altering the concentration of the ionic substances, and therefore the extent of the reverse action.*

#### DOUBLE DECOMPOSITION OF TWO SALTS. PRECIPITATION. CHEMICAL PROPERTIES OF IONIC SUBSTANCES

**Applications: Double Decomposition in Solution.**—We are now prepared to consider the general case of mixing the solutions of two ionogens.

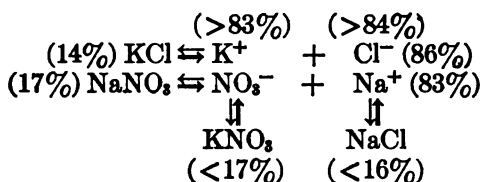
When solutions of two ionized substances are mixed, the first reflection which occurs to us is that each of these has been diluted by the water in which the other was dissolved, so that the first effect will be to increase the degree of ionization of both to a certain extent.

The next consideration is, however, that we have produced a mixture of four ions, which must have at least some tendency to unite crosswise. Thus potassium chloride and sodium nitrate in dilute solution are very greatly ionized before mixing. The reversible actions, represented by the horizontal pair of the following equations, have taken place extensively. But, by mixing the liquids, we have brought into presence of one another two new pairs of positive and negative ions. Hence, two other reversible actions, the vertical ones, will be set up and will proceed until a fresh equilibrium of all the ions with all four kinds of molecules has been reached. Thus far the description will fit any case of mixing solutions of two ionogens.



Now, in this particular instance, what is the actual extent of such interaction as has occurred? To answer this question we require to

know the proportion of molecules to ions in a solution of each of the four salts (p. 367). In decinormal solutions it is KCl, 14 : 86; NaNO<sub>3</sub>, 17 : 83; KNO<sub>3</sub>, 17 : 83, NaCl, 16 : 84, so that the salts are all equally well ionized. It is a good plan to add these proportions in the formulation, and to insert heavy arrows to indicate the preponderating direction in each equilibrium. Furthermore, in a *diluted* mixture, such as we are considering, the *proportions of ions are greater than these figures indicate*. Hence, practically no chemical action has occurred.



That this inference is correct is shown by independent evidence. Thus when the solutions of salts are mixed, and no precipitation occurs, **no thermal effect** is observable. This fact has been known since 1842 as Hess' law of **thermoneutrality**. There is also no change in color or in volume on mixing such solutions. Again, if the solutions (about  $N/4$ ) are placed in a cell (Fig. 106, p. 363), so that the one forms a layer below the other (the solution to be used for the lower layer is weighted with sugar), no change in conductivity is noticed when the solutions are stirred together. Hence no change in the number of ions has occurred.

We conclude, then, that when two highly ionized substances are mixed, **and the possible products are also highly ionized, soluble substances**, then **practically no chemical action occurs**. This rule applies to all soluble salts (p. 369) and to mixing salts with the highly ionized acids or bases.

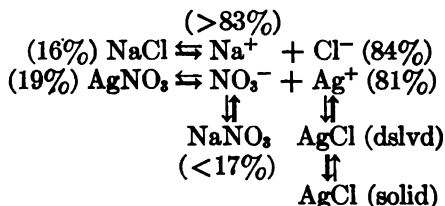
In view of the above explanation, the old question of whether such a solution contains the first pair of salts, or the second pair, represented in the double decomposition,  $\text{KCl} + \text{NaNO}_3 \rightleftharpoons \text{KNO}_3 + \text{NaCl}$ , loses its whole point. The solution contains neither the initial molecular substances nor the molecular products, in appreciable amount.

Conversely, when two ionized substances are mixed, **an extensive chemical change does ensue in two cases, namely:**

1. When one of the possible products is an insoluble substance and **precipitation** occurs, for this removes the ions used in forming the insoluble body.

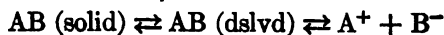
2. When one of the possible products, although soluble, is *little* ionized, as in *neutralization*, for this likewise removes the ions required to form molecules of the product. We proceed, therefore, to discuss these two important classes of actions.

**Precipitation.**—A typical case of precipitation occurs when we mix dilute solutions of silver nitrate and sodium chloride.



Here, since the four substances are all *salts*, they are all *highly* ionized. If they were all soluble, then, in dilute solutions, perhaps 5 per cent of each salt would be in molecules and the rest in ionic form. But the *molecules of silver chloride are excessively insoluble*. In all cases of precipitation, we look up the solubilities of the possible products (see Table of Solubilities, inside the front cover). Here we find that one liter of water will dissolve only 0.0016 g. silver chloride (this quantity includes *both* ions and molecules). So the concentration of the AgCl (dslvd) becomes almost zero through precipitation. So far as it is in solution, however, being a salt and very dilute, it is *practically all ionized*. The precipitation displaces the equilibrium, for, the dissociation having thus ceased, those of the ions  $\text{Ag}^+$  and  $\text{Cl}^-$  which combine are not replaced by others. Hence the silver-ion and chloride-ion almost disappear. This occurrence affects in turn the equilibria with  $\text{Na}^+$  and  $\text{NO}_3^-$ , so that the NaCl and  $\text{AgNO}_3$  become completely ionized. Hence the concentrations of NaCl and  $\text{AgNO}_3$ , of  $\text{Ag}^+$  and  $\text{Cl}^-$ , and of the dissolved AgCl, all become practically zero at last. The system finally contains only a precipitate of molecular, solid silver chloride and a solution of the three substances,  $\text{Na}^+ + \text{NO}_3^- \rightleftharpoons \text{NaNO}_3$ , in equilibrium. By far the greater part of this material in solution is the ionic, namely the  $\text{Na}^+$  and the  $\text{NO}_3^-$ .

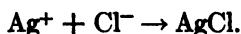
It will be noted that precipitation concerns only the *molecules*, directly, and that the ions, if there are any, are involved only indirectly. The ions are in equilibrium with the *dissolved* molecules, not with the precipitate.



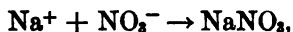
Hence, when a substance dissolves, it does so in molecular form, and ions are subsequently generated from some of these molecules until equilibrium is reached. Conversely, when molecules come out of solution, as the result of cooling or precipitation, the diminished concentration of the dissolved molecules enables more ions progressively to unite until the whole system has adjusted itself to the new conditions.

To avoid a misconception, note that the answer to the question, "Is silver chloride a highly ionized substance?" is "Yes." Since it is a salt, we expect this. True, very little of it dissolves, so that it cannot give many ions to a solution. But little or much ionized refers to the proportion ionized of the material which is in solution. With undissolved material ionization has nothing to do.

It should be noted that, when the solutions are mixed, as in the foregoing example, strictly speaking, the chief interaction taking place is the production of the *insoluble body*. The largest part of the chemical action may be formulated thus:



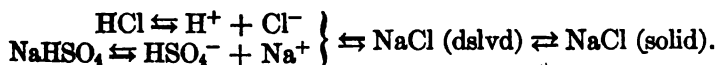
The chief change that has as yet befallen the ions of sodium nitrate is that they have been transferred from two separate vessels into one. Potentially the salt has been formed. But the actual union of its ions, to give the second product in the molecular condition,



comes about only when, at some subsequent time, if at all, the water is evaporated away.

The foregoing formulation and explanation apply to every case of mixing ionogens where precipitation occurs, that is, where the products are insoluble acids, bases or salts.

If the least soluble of the four salts is more soluble ~~than the others~~, chloride, more concentrated solutions are required to secure precipitation. The interaction of hydrogen chloride and sodium-hydrogen sulphate (p. 208) is of this nature:



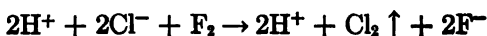
**Ionic Double Decomposition and Affinity.**—It is quite clear that the complete formation of acids, bases, and salts by precipitation is purely a result of mechanical details concerning solubility, and shows nothing about the degree of affinity between the

constituent ions. Again, the union of ions to form feebly ionized substances only shows the tendency of the *ionic* materials to unite, and may be complete where the free elements have little mutual affinity, and *vice versa*. Thus, hydrogen-ion and hypochlorite-ion  $\text{ClO}^-$  unite almost completely, while hydrogen-ion and chloride-ion hardly unite at all. Yet hypochlorous acid  $\text{HClO}$  is very unstable, while hydrogen chloride is just the reverse. Ionic double decompositions, consequently, give no clue to the activities of the free materials.

**Individual, Specific Chemical Properties of Each Ionic Material.** — We wrote the equation for the formation of silver chloride  $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$ , as if silver-ion and chloride-ion were the only substances concerned in the action. Further study shows this to be justifiable. Thus, hydrochloric acid, cupric chloride, and dozens of other chlorides may be used instead of sodium chloride and give silver chloride just as readily. The sodium-ion had nothing to do with the result. Of course we cannot get a solution containing chloride-ion alone. Like a vessel in which to make the experiment, some positive ion is required. But, like the rest of the apparatus, this ion may be varied indefinitely, is not altered in the course of the change, and may therefore be dispensed with in the equation. The nitrate-ion  $\text{NO}_3^-$  which accompanied the silver-ion is similarly a part of the apparatus, for silver sulphate solution works just as well as silver nitrate.

That chloride-ion is a substance with specific chemical properties, is easily demonstrated. It forms silver chloride whenever it encounters silver-ion. Other substances, even when they contain chlorine, lack this property. Chloroform  $\text{CHCl}_3$  and chlorobenzene  $\text{C}_6\text{H}_5\text{Cl}$ , in a solvent in which ionogens are dissociated, do not interact when silver nitrate is added. They give no chloride-ion and, in fact, remain un-ionized. Potassium chlorate  $\text{KClO}_3$  and perchlorate  $\text{KClO}_4$  and chloroacetic acid  $\text{HCO}_2\text{CH}_2\text{Cl}$ , with silver-ion, fail likewise to give silver chloride. They are ionized, but chloride-ion is not one of the ions of any of them. The ions  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ , and  $\text{CO}_2\text{CH}_2\text{Cl}^-$ , have properties of their own, and their compounds with silver-ion are soluble.

Other chemical properties of chloride-ion are: That it unites also with lead-ion  $\text{Pb}^{++}$  and mercurous-ion  $\text{Hg}^+$ , forming insoluble chlorides (p. 226). It is discharged and liberated as free chlorine by fluorine (p. 281):



Since the hydrogen-ion is not affected and other chlorides behave in a similar manner, the positive ion may be omitted:  $2\text{Cl}^- + \text{F}_2 \rightarrow \text{Cl}_2 + 2\text{F}^-$ .

Finally, chloride-ion has relatively little tendency to unite with other ions, or, in other words, the compounds of chloride-ion with most other ions are highly ionized. Thus it combines with hydrogen-ion to the extent of only 8 per cent (p. 377) in decinormal solution. In this respect it differs markedly from *free* chlorine, just as hydrogen-ion differs from hydrogen. The free elements unite with vigor and completely. Hydrogen chloride is easy to dissociate into ions, but difficult to dissociate into its constituent elements. Nothing could show more strikingly than this that the ionic materials have chemical properties of their own.

Similarly, barium salts and ordinary sulphates give, when mixed, a precipitate of barium sulphate  $\text{BaSO}_4$ . Here we encounter a property of barium-ion  $\text{Ba}^{++}$  and sulphate-ion  $\text{SO}_4^{--}$ . But potassium-ethyl sulphate  $\text{KC}_2\text{H}_5\text{SO}_4$ , in spite of its name, will not give this reaction with a barium salt. Here electrolysis shows that sulphate-ion is absent and that the negative ion is  $\text{C}_2\text{H}_5\text{SO}_4^-$ .

In the same way every other ionic material may be shown to be a substance with an individual set of physical (p. 375) and chemical properties. Each salt, when dissolved, gives two kinds (at least) of ionic materials. The solution is simply a mixture, and each physical component forthwith behaves, towards ions capable of uniting with it, as if it were alone. The other materials, ionic and molecular, which are present, may remain essentially unaffected throughout the change.

**Application in Chemical Analysis.**— Since the larger number of ordinary chemical substances are ionogens, and the most rapid and simplest chemical changes take place when they are in solution, the various reactions of their solutions are employed as tests for the substances in question. An advantage of the use of the solutions is that they contain a mixture of two independent materials, the anion and the cation, and when these have been identified successfully the salt from which they were formed is known. The simplicity to which chemical analysis is thus reduced may be seen when we consider that twenty-five common metals with twenty-five negative radicals might give a total of over six hundred different salts. If the distinct properties of *each* of these had to be considered, the identification of an unknown substance would be very difficult. In solution, how-



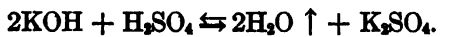
ever, the problem becomes much easier. Every solution made from a single salt will contain but two substances (in the main; see, however, below), and the problem reduces itself to ascertaining which two, out of a total of fifty, are present in any particular case. This is easier than investigating six hundred possibilities.

As an example of the method, let us suppose that we look first for the positive ion. Most systems of analysis begin by the addition of a solution containing chloride-ion, generally dilute hydrochloric acid, to the liquid. If an ion is present which in combination with chloride-ion gives an insoluble compound, a precipitate will appear. Amongst the common positive ions but three are of this kind, namely, silver-ion, mercurous-ion, and lead-ion. So that the precipitate, if it appears, is a chloride of one of these three metals, and the matter of distinguishing between the three is quickly disposed of by further examination of its properties. If no precipitate comes out, then these three metals are probably absent, and some fresh ion capable of precipitating another set of positive ions is introduced (see Chap. XXXVII). Thus by a process of elimination we quickly find out whether any metal ion is present, and, if so, precisely which one it is.

The language of analysis is frequently somewhat loose. Thus we speak of the addition of a silver salt to a solution as being a "test for chlorine." As a matter of fact, it is not a test for chlorine. It is not intended as a test for free chlorine, nor will it show the presence of chlorine in many states of combination. It is simply a test for ionic chlorine  $\text{Cl}^-$ , and cannot give us information in regard to the presence or absence of any other form of the element. So the wet-way tests for "copper," "silver," etc., so called, are tests for the ionic forms of these elements, and not for the presence of the element in every form. Even the two kinds of copper and mercury ions,  $\text{Cu}^{++}$ ,  $\text{Cu}^+$ ,  $\text{Hg}^{++}$ ,  $\text{Hg}^+$ , must be classed as distinct substances. Thus, the last is precipitated by chloride-ion while the second last is not, mercuric chloride  $\text{HgCl}_2$  being soluble.

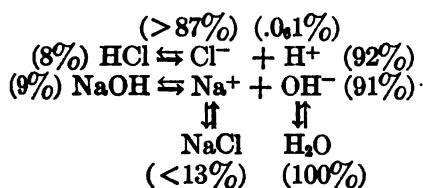
### NEUTRALIZATION

**Neutralization.** — When 80 per cent sulphuric acid is poured upon solid potassium hydroxide, much heat is developed and clouds of steam arise. The solid product, when freed from the rest of the water, is potassium sulphate:



With any other pair consisting of an acid and a base, a similar interaction occurs (*cf.* p. 213), water and a salt being produced.

A double decomposition between ionogens is always reversible (p. 380), and so we should expect that *in dilute solution* the interaction of an acid and a base would be incomplete. We find, however, that this particular sort of action almost always goes to completion. This kind of action is called **neutralization**, because both acid and base are completely consumed, and hydrogen-ion and hydroxide-ion are alike impossible of detection in the resulting mixture. The solution is **neutral** to litmus.



The general plan of all interactions of acids and bases is shown in the formulation. The ionization of the hydrochloric acid reaches 0.92 in a decinormal solution, and goes farther when the acid is diluted

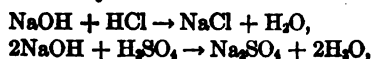
with the water of another solution. That of the sodium hydroxide similarly goes beyond 0.91. Thus the substances in the solutions before mixing are almost entirely ionic. The crosswise union,  $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$ , however, is all but complete, for water is hardly ionized at all (p. 367). The materials on whose interaction with the  $\text{Cl}^-$  and  $\text{Na}^+$ , respectively, the maintenance of molecules HCl and NaOH depends, being thus removed, the dissociation of the acid and base promptly brings itself to completion, and the left sides of the equations vanish. Practically all the hydrogen-ion and hydroxide-ion become water, which thenceforth is simply a part of the solvent. The  $\text{Cl}^-$  and  $\text{Na}^+$ , however, if the solution is now 1/20 normal, unite to the extent of 0.13 only. If it is more dilute, this union forms a still smaller factor in the whole change. Practically it is negligible. Now all that has been said of this acid and base will apply *mutatis mutandis* whenever any active, highly ionized acid and base come together. Thus we may write one simple equation for all neutralizations of active acids and bases:



without omitting anything essential.

The ions of a salt are always left over from the main action, and may be brought together, in turn, by evaporation:  $\text{Na}^+ + \text{Cl}^- \rightarrow \text{NaCl}$ , or the liquid may be used as a solution of the pure salt.

The equations as commonly written:



apply to the interactions when water is absent. If used for neutralization in dilute solution, it must be understood that they condense two changes into one equation. The formation of water comes first, that of the salt afterwards. Sometimes neutralization is wholly misconstrued by the supposition being made that it occurs in consequence of a great tendency to salt formation.

**Confirmations of this View of Neutralization.**—The neutral mixture of the acid and base gives no evidence of the presence either of the hydrogen ions or of the hydroxide ions. The characteristic tastes, and actions upon indicators, of these two ions, and the interaction of the former of the two with metals like magnesium, are all wanting. That this is due, not simply to two opposing influences having destroyed each other's effects, but to a real disappearance of the agencies themselves, may be demonstrated by showing that the total number of ions is very much smaller in the mixture than in the two substances taken separately.

The trough (Fig. 106, p. 363) is half-filled with a dilute solution (say,  $N/4$ ) of some active acid, such as hydrochloric acid. An equal volume of a  $N/4$  solution of some soluble base (loaded with sugar), such as sodium hydroxide, is then allowed to flow in, below the acid. On completing the circuit we find a considerable deflection of the amperemeter (say, 1.5 amperes). When the interaction is now brought about by stirring, a very great fall in the reading (say to 0.5 amperes) is observed.\* The only plausible explanation is that, not only have many of the ions assumed a molecular form, but those which have suffered in this respect have been the most rapidly moving and best conducting ones, namely, the hydrogen-ion and hydroxide-ion.

Again, a considerable thermal effect accompanies neutralization. But, in the cases we are discussing, that is where *active* bases and acids are employed, the heat liberated by use of equivalent weights (p. 182) is *always the same*, namely 13,700 cal. That it is always the same confirms our theory, for practically the whole change is always the formation of 18 g. of water from the ions.

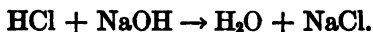
When less highly ionized acids or bases are used, the only differ-

\* The experiment may be made more striking by adding a few drops of phenolphthalein solution to the acid and using a *minute* excess of the base. To prevent the appearance of a pink layer at the interface, and before the stirring, a thin layer of sodium chloride solution (loaded with less sugar than the solution of the base) may be introduced below the acid, before the layer of the base is added.

ence is that there are more of the molecular materials present, before the solutions are mixed. But the removal of the  $H^+$  and  $OH^-$  ions permits the molecules of the acid and base to dissociate, so that the final products are water and the ions of a salt, as before. This case is discussed in detail later.

The foregoing formulation and explanation apply to every case of mixing ionogens, where a very slightly ionized substance is one of the products, that is, when water, or a feeble acid, or a feeble base (pp. 369-370) is formed.

**Acidimetry and Alkalimetry.**—When, as is constantly the case, a chemist desires to ascertain the quantity of an acid or base present in a solution, he uses for the purpose the interaction just discussed. If, for example, the problem is to ascertain the weight of hydrogen chloride per liter in a specimen of hydrochloric acid, this can be done by neutralizing a measured portion of this acid with a solution of an alkali of *known concentration* (see next section). The volume of the latter which is required for the purpose is observed. If the alkali is sodium hydroxide, the action taking place is



The volume of acid is measured out into a beaker by means of a pipette (Fig. 107) of fixed capacity, which is filled by suction to the mark on the stem. Suppose the amount to be 25 c.c. The standard alkali solution is placed in a burette (Fig. 108), which is filled down to the tip of the nozzle. A few drops of litmus solution are now added to the acid, the level of the alkali in the burette is read off, and the alkali is allowed to run slowly into the acid. After a time, the hydroxide-ion which this introduces will begin to produce a blue color, close to where the stream enters the liquid. This is at first dissipated by stirring, and the whole remains red. Finally, however, a point is reached at which the entire solution assumes a tint intermediate between blue and red. With one drop less of the base, it is distinctly red. With one drop more, it would become distinctly blue. Litmus paper of either shade dipped in this neutral solution remains unaffected. The level in the burette is read again, and the difference between this and the previous reading gives the number of c.c. of standard alkali used.

By the use of a standard solution of an acid in the burette, the quantity of a base may be determined in the same way.



FIG. 107.

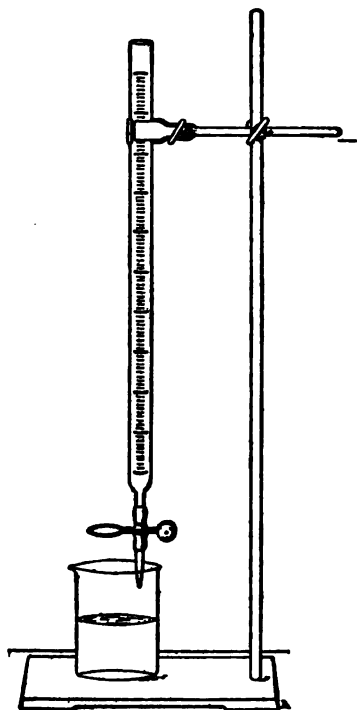


FIG. 108.

**Standard Solutions.**—The standard solutions used in this work are usually normal, and contain one equivalent weight of the alkali or acid in one liter of the solution. For more delicate work, decinormal ( $N/10$ ) solutions may be employed. The concentration of such a solution is called its **titer**, and the operation of analyzing another solution by means of it, **titration**. The value of standard solutions lies in the fact that, when once the solution has been prepared, and the exact concentration adjusted by quantitative experiments, its use does not require any weighing, and the measurements of volumes can be carried out with great rapidity. A process involving weighing need not again be undertaken until the stock of the standard solution is exhausted.

The calculation of the result is also simple. One liter of normal

alkali contains 17 g. of available hydroxyl, and one liter of normal acid, 1 g. of available hydrogen (p. 182). Equal volumes of normal solutions will therefore exactly neutralize one another, 18 g. of water being formed by interaction of a liter of each. If, for the neutralization of the 25 c.c. of hydrochloric acid used above, 50 c.c. of normal alkali are required, the acid is twice-normal (2N). When 15 c.c. are required, the acid is  $\frac{2}{3}$  or  $\frac{2}{3}$ N. If the actual weight of the acid in the latter case has to be calculated, we remember that there are 36.46 g. of hydrogen chloride in 1 l. of a normal solution, and therefore  $36.46 \times \frac{2}{3} \times \frac{1}{1000}$  g. = 0.5467 g. in 25 c.c. of a solution which is  $\frac{2}{3}$ -normal.

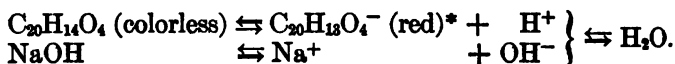
Methods of quantitative analysis in which standard solutions are employed are known as **volumetric** methods, and are much used by analysts and investigators. They occupy much less time than **gravimetric** operations, in which numerous weighings have to be made, and are often just as accurate. The substances, like litmus, by whose change of color the completeness of the action is made known, are called **indicators** (see below).

**Indicators.** — Indicators are substances which, in presence of certain other substances, assume a very deep color, or change sharply from one deep color to another. Thus, phenolphthaleïn (p. 388) is colorless in presence of acids (*i.e.*, hydrogen-ion), and red (when dilute, pink) in presence of alkalies (*i.e.*, hydroxide-ion). Litmus, again, is red with acids, and blue with alkalies. The change of color depends upon a chemical interaction in each case, but since indicators are chosen for their strong coloration, the quantity of the acid or base used up in changing the tint of the trace of the indicator is so small as to be negligible. The common indicators are:

**Phenolphthaleïn**  $C_{20}H_{14}O_4$ , a colorless substance and very feeble acid. It is not perceptibly dissociated into its ions:



and in neutral or acid solutions is, therefore, without visible color. When a base is added gradually to an acid containing some of this indicator, the acid is first neutralized. Then, and not till then, the slightest excess of hydroxide-ion unites with the trace of hydrogen-ion from the phenolphthaleïn, the above equilibrium is displaced forwards, and a visible amount of the red negative ion is formed:



In this more compact formulation, we show the product ( $\text{H}_2\text{O}$ ) from the union of the two ions which combine, but omit the product from the union of  $\text{Na}^+$  and  $\text{C}_{20}\text{H}_{13}\text{O}_4^-$ , because here (since the product is a salt) hardly any union occurs.

This indicator is especially sensitive to acids (weak or strong),† and it shows the presence of an excess of alkali most sharply when the alkali is an active one like sodium hydroxide, and should, therefore, be employed only with strong bases. With a weak base like ammonium hydroxide, a considerable excess of the base must often be used before the color appears.

**Litmus** is an extract from certain lichens, first used by Boyle. It contains azolitmin. One of its colors is that of the molecule, and the other that of the ion.

**Methyl orange**,  $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{N}:\text{N}:\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ , is a complex organic compound which gives, in acid solution, a red and in alkaline solution a yellow color. This indicator is very sensitive to bases, both strong and weak.†

**Congo red** is the sodium salt of an acid of complex structure (see Dyes). In neutral or alkaline solutions it is red; with acids it turns blue. Paper dipped in Congo red differs from litmus paper in that it shows gradations in color, the blue being much more distinct with an active acid than with a relatively weak one like acetic acid (p. 369). Litmus paper is equally red with all acids save the very feeblest.

Some special indicators have been mentioned. Thus, starch emulsion is used for recognizing the presence of traces of iodine (p. 276). Potassium permanganate is itself so strongly colored that it is its own indicator (p. 320).

### WEAK ACIDS AND BASES

**Active and Weak Acids.**—In solutions containing equivalent quantities of hydrogen salts, and therefore equal amounts of com-

\* The ion has this composition, but, in reality, has a different chemical structure from the corresponding part of the original molecule. An internal rearrangement, not representable in the equation, accompanies the dissociation. The same remark applies to the other indicators.

† A neutral solution contains  $\text{H}^+$  and  $\text{OH}^-$  in the same concentrations as in water, namely  $0.041N$ . Methyl orange becomes yellow with  $0.041N \text{H}^+$ , and phenolphthalein becomes colorless when  $\text{OH}^-$  becomes  $0.041N$ .

*bined* hydrogen, in equal volumes, the concentration of hydrogen-ion at any moment in each will be different. This concentration will be high or low according to the extent to which water is able to dissociate the molecules. Now the activity of the hydrogen-ion, that is, the speed with which it will interact, like that of any other substance, depends on its concentration (p. 292). Hence the hydrogen salts furnish, on being dissolved, acids of all degrees of activity. Thus in normal hydrochloric acid, the fraction dissociated is 0.78, and the hydrogen-ion is 0.78-normal, whereas in normal acetic acid the hydrogen-ion is only 0.004-normal (p. 366). Yet the amounts of hydrogen chloride and hydrogen acetate per liter contain equal quantities of replaceable hydrogen, namely, 1 g. each. Both the solutions in fact are normal in respect to combined hydrogen. But the normal acetic acid has only about one two-hundredth of the activity of normal hydrochloric acid.

That a difference in the activity of different acids does exist may be shown, roughly, by placing similar pieces of the same metal, say zinc, in equal volumes of various normal solutions of acids, such as hydrochloric, sulphuric, and acetic. The hydrogen is evolved more rapidly by the first than by the second, and very much faster by either than by the last. Naturally, the first is sooner exhausted, while the third acts in its slow way for a very long time before being all used up. In the third case few ions of hydrogen are at hand at any one moment, but more are formed continuously from the molecules, to take the place of those displaced. Thus the total amount of hydrogen obtained from each acid is finally the same. It is *the speed of evolution alone which is different* and shows the differing concentrations of the hydrogen-ion.

In cases of extremely small ionization, the presence or absence of visible action on litmus may form another means of estimating activity. Thus, litmus is *easily* turned red by a deci-normal solution of acetic acid or of any more active acid (p. 369), but hydrogen sulphide, in a solution of the same molecular concentration, contains only one-twentieth as many hydrogen ions (p. 369), and affects litmus paper but slightly. Paper dipped in Congo red exhibits differences in the activity of acids by the different depths of the tints it assumes. For example, it is much less markedly affected by acetic than by sulphuric acid of the same concentration (Indicators, p. 392).

Many hydrogen salts are but slightly soluble. Thus, with silicic acid (*q.v.*), the solid can keep only a small concentration of molecules in solution:  $\text{H}_2\text{SiO}_3$  (solid)  $\rightleftharpoons$   $\text{H}_2\text{SiO}_3$  (dissd). So that, although



some ions are doubtless present,  $\text{H}_2\text{SiO}_3$  (dsldv)  $\rightleftharpoons 2\text{H}^+ + \text{SiO}_3^{--}$ , their concentration, being dependent on that of the molecules, is very minute indeed. Still, even in the absence of an effect upon litmus, the substance can be recognized to be an acid. Thus, by the action of sodium hydroxide, silicic acid can be made into sodium silicate  $\text{Na}_2\text{SiO}_3$ , which is highly soluble and highly ionized. Hence, since  $\text{SiO}_3^{--}$  is a negative ion, we reach the conclusion indirectly that  $\text{H}_2\text{SiO}_3$  is an acid.

Substances like ammonia  $\text{NH}_3$ , sugar, and alcohol, although they contain hydrogen, are not hydrogen salts. They are not ionogens (cf. p. 342), and give no hydrogen-ion. Ionizable and non-ionizable hydrogen may even be contained in the same compound. Thus, each molecule of acetic acid  $\text{H}.\text{CO}_2\text{CH}_3$  contains four hydrogen units, but gives only one hydrogen ion. The other three are part of the acetate-ion  $\text{CO}_2\text{CH}_3^-$ . We infer this because metals can be substituted for one hydrogen unit ( $\text{NaCO}_2\text{CH}_3$ ), but not more.

**Active and Weak Bases.** — The case of **weak bases** is exactly analogous to that of weak acids. Thus, in normal potassium hydroxide  $\text{KOH}$ , the fraction ionized is 0.77 and the hydroxide-ion  $\text{OH}^-$  is 0.77-normal, whereas in normal ammonium hydroxide  $\text{NH}_4\text{OH}$  the hydroxide-ion is only 0.004-normal. Yet both solutions are normal in respect to ionized and combined hydroxyl together. But normal ammonium hydroxide has only about one-one hundred and ninetieth of the basic activity of normal potassium hydroxide.

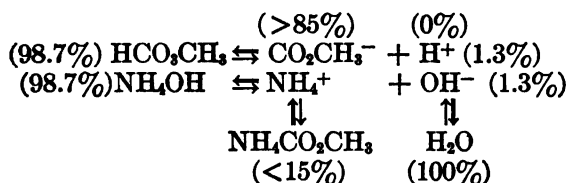
Most bases, as we have seen (p. 374), are but slightly soluble, and do not give sufficient hydroxide-ion to affect indicators. Yet they interact with acids, often giving soluble, and in all cases highly ionized salts.

Trinitrobenzene  $\text{C}_6\text{H}_3(\text{NO}_2)_3$ , which is colorless in acid solution and deep-orange in presence of an active base, can be used to show different concentrations of hydroxide-ion. Thus, with *N*-sodium hydroxide it gives a dark orange color (0.73*N*  $\text{OH}^-$ ), but with a *N*/10 solution light orange (0.091*N*  $\text{OH}^-$ ). With *N*-ammonium hydroxide it gives a very faint color (0.004*N*  $\text{OH}^-$ ) and with a *N*/10 solution no color (0.0013*N*  $\text{OH}^-$ ).

**Neutralization of Little Ionized Substances.** — When concentrated solutions are employed, or, when acids and bases which are but little ionized are involved, the mechanism of the change is still the same in all respects. The only difference is that, since the acid or

base is not fully ionized to start with, its molecules must dissociate progressively, in proportion as the hydrogen ions pass into combination. All the hydrogen and hydroxyl capable of forming ions will pass through that stage, and ultimately become water, before the solution can reach the neutral condition.

The neutralization of inactive bases and acids gives instructive results, when performed in the conductivity trough (Fig. 106, p. 363). Thus, if the trough be first half-filled with  $N/10$  acetic acid, and an equal volume of  $N/10$  ammonium hydroxide (loaded with sugar) be run in below the acid, the formulation (two horizontal lines) shows the degrees of ionization:

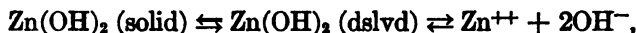


The conductivity before mixing (horizontal lines) is very slight. After mixing, water, which is hardly ionized at all, and ammonium acetate, a highly ionized salt are formed. On the whole, the number of ions is greatly increased, and the conductivity increases also very markedly.

From all this it will be seen that the *activity* of acids and bases cannot be measured by the *quantity* of base or acid required to neutralize them. The full amount required by the equation is always needed in every case. This is because neutralization uses up the hydrogen- or hydroxide-ion *at once*, and so permits the rapid generation of a fresh supply. The concentration of one of these ionic materials can only be measured by some action which uses it up slowly or not at all, so that ionic double decompositions are excluded. In the action of metals on acids (p. 128), and in determining conductivity (p. 362), the consumption of the ions is slow, and hence the measurement can be made in these cases. Actions which consume no ions at all are also known, and are used in measuring activity (see Carbohydrates and esters).

The reader must *not* fall into the error of supposing that the neutralization of inactive bases and acids *takes a longer time* than that of active ones. The formation of more ions, by the ionization of the molecules, is so rapid that the time it occupies is in *all* cases too short to be measured. Ionization appears to be instantaneous.

When the acid or base is but little soluble in water, as when zinc hydroxide is treated with a dilute acid, one other link is added to the network of equilibria. The acid proceeds to interact with the small dissolved part of the base. As this is disposed of, solution goes on progressively and, through a train of equilibria:



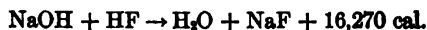
the supply of hydroxide-ion is maintained until all the molecules of the base, solid and dissolved, are used up and the action is completed. Heating hastens these, as it does all other changes.

If acid and base are alike insoluble, it saves time, if the production of the salt is the ultimate object, to fuse the materials together at a high temperature.

**Thermochemistry of Neutralization.**—The above interpretation of the phenomena of neutralization is confirmed by many facts. Thus a considerable amount of heat is liberated in neutralization. Now, as we have seen (p. 388), when **active acids** (p. 373) and **bases** (p. 374) in dilute solution are concerned, it is found that the quantities of heat for the neutralization of the same amount of hydrogen-ion, or hydroxide-ion, are **always the same**, namely, 13,700 cal. for equivalent weights. If the action consisted primarily in the formation of a different salt from every pair, we should expect the heat liberated to be different. Thus, the heats of formation of dry potassium chloride and dry sodium iodide are 104,300 cal. and 69,100 cal., respectively. But the heats of formation of their solutions by neutralizing the proper acids and bases are identical. If, however, in such cases, neutralization consists always simply in the formation of water, we should expect the quantities of heat liberated to be identical, as, in fact, they are:



We are confirmed in these conclusions when we employ concentrated solutions, or use less completely ionized, or insoluble acids and bases for neutralization. With such substances—and they are in the majority—the heats of neutralization are not alike, but different in every case. Thus, for dilute solutions of sodium hydroxide and hydrofluoric acid, the latter a slightly ionized, soluble acid, the thermochemical equation is as follows:

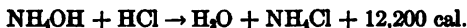


Since the sodium fluoride is fully ionized, the only difference between this case and the preceding one is that the hydrogen fluoride is largely in the *molecular* condi-

tion to start with, and that here, in addition to the union of hydrogen and hydroxyl ions, we have a continuous dissociation of the hydrofluoric acid accompanying the neutralization. The fact that here the heat produced is much greater than before, shows that the dissociation of this acid is associated with the *production* of heat (*cf.* pp. 305, 368). When the same base is used with hypochlorous acid, the divergence is in precisely the opposite direction and about the same in amount:



Here again the salt produced, sodium hypochlorite, is fully ionized, so that the diminished evolution of heat must be due to the fact that the feebly ionized hypochlorous acid (in *N*/10 solution, only 0.0002 ionized) *absorbs* part of the heat of neutralization in passing into the ionic condition. Applying this to bases, we find that the neutralization of ammonium hydroxide, a feebly ionized base, with any active acid, gives a heat of neutralization below the normal:



Here again the salt produced is fully ionized. Thus the ionization of the ammonium hydroxide must have consumed an appreciable part of the heat of neutralization which would otherwise have reached the normal figure of 13,700 calories.

**Volume Change in Neutralization.** — When the volumes of the solutions of *active* acids and alkalies are carefully measured before being mixed, and compared with the volume of the neutral mixture, an expansion is always found to have occurred. When one liter of a normal solution of each substance is taken at starting, the volume of the mixture is always 20 c.c. greater than that of the component liquids. This is rather remarkable, because the chemical change has produced only 18 c.c. of water, yet the volume of the water appears to be 20 c.c. *greater* than that of the ions from which it was formed. This shows that the change involves more than the mere union of the ions. The electric charges on the ions cause a high internal pressure, called **electrostriction**, especially in the molecules of water immediately surrounding each ion, and the liquid is compressed. When the ions unite, the pressure is removed, and expansion occurs. When less highly ionized acids and bases are used, the alteration in volume is irregular, since it is affected by the occurrence of other changes than the mere union of hydrogen-ion and hydroxide-ion.

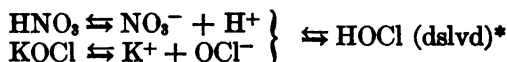
**Interaction of Salts with Acids and Bases.** — When a highly ionized acid is mixed with a salt, a reversible action tending to form another acid and salt is set up. Such an action is that of nitric acid on a hypochlorite in dilute solution:



giving potassium nitrate and hypochlorous acid. In such a case, if the products are both as highly ionized as the initial substances, the

result is similar to that of the interaction between potassium chloride and sodium nitrate (p. 381). No decisive change takes place.

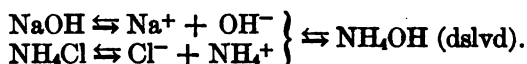
With hypochlorous acid, however, which is very slightly ionized (0.02 per cent in *N*/10 solution), the result is different:



This acid is promptly formed from its ions, and the final mixture contains, mainly,  $\text{K}^+$ ,  $\text{NO}_3^-$  and molecular  $\text{HOC}$ . Yet, since the substance is soluble, no outward evidence that the action differs from that of potassium chloride and sodium nitrate is visible. The conductivity, however, is found to have been greatly reduced when the solutions are mixed (p. 388), because half the ions, including the most rapidly migrating of the four (hydrogen-ion), have been removed (p. 347). The action of an active acid upon a solution of sodium peroxide (p. 315) is another illustration of this sort of action.

When the molecules of the resulting acid are insoluble, then it may be precipitated (*cf.* silicic acid), after the manner of silver chloride (p. 382), or may escape, if an insoluble gas (*cf.* hydrogen sulphide), irrespective of its degree of ionization.

In the same way, when a salt and a base are brought together, a base and a salt are produced. All that has been said in the preceding paragraph applies to this case also. Thus ammonium hydroxide (*q.v.*), which is a feebly ionized base (p. 370), is formed on this plan, by mixing solutions of an ammonium salt and a strong base:

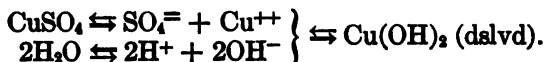


When the resulting base is insoluble, like zinc hydroxide, it is precipitated, and the action becomes nearly complete on this account and irrespective of the degree of ionization.

**Interaction of Salts with Water: Hydrolysis.** — The natural ionization of water is very slight, but there are cases in which its effects become noticeable, and the interaction of its ions with those of dissolved salts cannot be neglected. For example, an aqueous

\* To save space, this mode of formulation (p. 392) will be used when there is very complete union of only one pair of the ions. Here the  $\text{K}^+$  and  $\text{NO}_3^-$ , being the ions of a salt, combine to a very slight extent only.

solution of pure cupric sulphate is always acid and therefore contains excess of hydrogen-ion:



Cupric hydroxide, being a very feeble base, and comparable with water itself in the small extent to which the solvent is able to hold its ions apart, is formed to a small extent. The removal of some hydroxide-ion by this means enables more of the water to dissociate. This in turn furnishes the material for the production of more cupric hydroxide. The action does not proceed very far, but it makes sufficient progress to leave a perceptible excess of hydrogen-ion in the liquid and to give it, therefore, an acid reaction. The hydrogen-ion combines slightly, but only slightly, with the sulphate-ion, for sulphuric acid is a highly ionized acid. This part of the action has, therefore, been left out of the diagram. The ordinary equation for this change would be:



The hydrolysis is much greater with sodium sulphide (*q.v.*) and antimony trichloride (*q.v.*).

Again, soap solution is always faintly alkaline:



The sodium palmitate is highly ionized, but palmitic acid  $\text{HC}_{15}\text{H}_{31}\text{CO}_2$  is hardly ionized at all. The final result is the production of a recognizable amount of hydroxide-ion in the solution. Thus, a salt derived from an acid and a base of very different degrees of activity, whether it is the base (as  $\text{Cu}(\text{OH})_2$ ) or the acid (as palmitic acid or hydrogen sulphide, *q.v.*) which is the weaker member, is likely to be more or less hydrolyzed by water. In the former case the solution is acid, in the latter basic in reaction. When *both* the acid and the base are weak, the hydrolysis is more extensive. Other things being equal, salts containing bivalent or trivalent radicals are more noticeably hydrolyzed than are those composed only of univalent radicals.

It will be seen that hydrolysis is the precise reverse of neutralization (pp. 389, 395). The latter being almost always nearly complete, the former must be, as a rule, very slight.

Cases of this kind being common, we are thus compelled to enlarge our list of possible components in the solution of any salt (*cf.* 375).

In addition to the molecules and ions of the salt, there are present, water and its ions, and the molecules of the base and acid formed by the union of the latter ions with the former. There are thus no less than **eight different components** in the mixture.

### MIXED IONOGENS AND DOUBLE SALTS

As a rule, a univalent ion, such as chlorate-ion  $\text{ClO}_3^-$ , unites with one kind of cation to give but one kind of salt. The result is called a **neutral or normal salt**, as  $\text{KClO}_3$  or  $\text{NaClO}_3$ . The acid, chloric acid, is called a **monobasic acid**, for its molecule reacts with but one molecule of a base. The possibilities are more numerous, however, with an ion of higher valence. Thus:

#### CARBONATE-ION MAY GIVE:

$\text{H}_2\text{CO}_3$ , the acid,  
 $\text{Na}_2\text{CO}_3$ , a neutral salt,  
 $\text{NaHCO}_3$ , an acid salt,  
 $\text{NaKCO}_3$ , a mixed salt,

#### CALCIUM-ION MAY GIVE:

$\text{Ca}(\text{OH})_2$ , the base,  
 $\text{CaCl}_2$ , a neutral salt,  
 $\text{Ca}(\text{OH})\text{Cl}$ , a basic salt,\*  
 $\text{CaCl}(\text{OCl})$ , a mixed salt.

Carbonic acid is a di-basic acid, and calcium hydroxide a di-acid base. The last two compounds of each set are mixed ionogens. Their characteristic is that they contain more than two kinds of radicals and break up in solution, giving more than two kinds of ions.

**Acid Salts.** — The acid salts may be obtained by using half that quantity of the base which would be required fully to neutralize the acid, and evaporating the resulting solution:



With a monobasic acid, say hydrochloric acid, this treatment gives simply a mixture of the normal salt and the free acid, and not a single substance.

Acid salts are also formed by the interaction of other salts with an excess of the acid (pp. 206, 207).

The **acid salt** is intermediate in composition between the acid itself and the normal salt. All of the hydrogen of the acid has not been displaced by the metal. It is named an acid salt on account of its composition, but is not necessarily acid in its reaction towards litmus. That depends on whether its solution contains a sufficient amount of hydrogen-ion to affect indicators. Sodium-hydrogen sulphate gives the ions  $\text{Na}^+$  and  $\text{HSO}_4^-$ , but, even in moderately dilute

\* This particular basic salt has not been isolated in a pure state.

solution, the latter ion is further dissociated into  $H^+$  and  $SO_4^{=}$  to a large extent (p. 367). Its solution is therefore acid in truth. On the other hand, sodium-hydrogen carbonate  $NaHCO_3$ , derived from carbonic acid,  $H_2CO_3$ , gives the ions  $Na^+$  and  $HCO_3^-$ , and the amount of hydrogen-ion formed by the latter is too small to be detected by indicators. This acid salt gives therefore a solution which is actually neutral to litmus.\*

**Basic Salts.** — Corresponding to the acid salts we have also basic salts, about which statements parallel to the above might be made. Thus, from sodium hydroxide but one salt can be formed. With lead hydroxide,  $Pb(OH)_2$ , however, the displacement of one hydroxyl by a negative radical, without the disturbance of the other, is conceivable and can be achieved. The half-chloride, for example, is called lead oxychloride  $Pb(OH)Cl$ . The basic salts are usually insoluble in water, and therefore as a rule do not exhibit the basic reaction with litmus.

**Mixed Salts.** — So-called mixed salts, like sodium-potassium carbonate  $KNaCO_3$  (see Silicates), may be obtained by half neutralizing the acid with the calculated amount of one base and then completing the operation with the other. Corresponding treatment will give mixed salts of a di-acid base.

It will be seen that  $2KNaCO_3$  is equivalent to  $K_2CO_3, Na_2CO_3$ , and that  $2CaCl(OCl)$  is equivalent to  $CaCl_2, Ca(OCl)_2$ . Since we have as yet no general means of determining the molecular weights of solids, there is no generally applicable way of deciding which formula is preferable (see, however, Bleaching powder, p. 475, and under Calcium). In solutions of these salts the ions which are found might come from a substance possessing either of the alternative formulæ, so that no light is thrown on the question by this means. Thus, most compounds of this kind, with the exception of acid and basic salts,† are considered to be molecular compounds (p. 154) of two salts and are classed as double salts.

\* Because of hydrolysis (p. 398), the solution of the "neutral" salt, sodium carbonate  $Na_2CO_3$ , is actually *alkaline* in reaction. The terms "acid," "basic," and "neutral," applied to salts, refer simply to the composition and ignore the behavior.

† The formulæ of basic salts even are often written as if such salts were molecular compounds, as  $Cu(OH)_2, CuCl_2$ , or even  $CuO, CuCl_2, H_2O$ , in place of  $Cu(OH)Cl$  (see Copper).



**Double Salts.** — Substances similar to ferrous-ammonium sulphate  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , and alum (*q.v.*), are very numerous. Because their formulæ can be written so as to show two complete salts, and because they are easily formed by crystallization from a solution containing both salts, they are called **double salts**. In solution they are resolved into their constituent salts, and these, in turn, are ionized. Almost always the acid radicals are identical (see, however, Kainite).

Each kind of ion of a double salt exhibits its own properties, irrespective of the nature of the numerous substances, ionic and otherwise, which are present. Hence, when a solution of a particular ionic material is required, solutions of such bodies are often used instead of those of simpler ones, if for any reason the substitution is convenient. The choice of the complex compound must be made in such a way that the other ions shall not interfere with that particular reaction of one of them which is in question.

The class of bodies known as *salts of complex acids* (*q.v.*) are ionized like ordinary salts and not like double salts.

#### KINDS OF IONIC CHEMICAL CHANGE

Five distinct varieties of chemical change are characteristic of ionic materials. These are: (1) Disunion or combination of ions, (2) displacement of the material of one ion by another substance, (3) destruction or formation of a compound ionic material, (4) change in the charges of two ionic materials, (5) charge or discharge of two ionic materials, in electrolysis. Every one of these kinds of action has been illustrated, some of them very frequently, in the present and foregoing chapters.

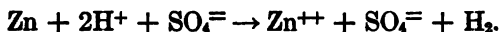
**1. Disunion and Combination of Ions.** — This sort of change is illustrated every time an ionogen is dissolved in water (disunion) or a solution of such a substance is evaporated (combination). Both of the directions of this sort of change occur also to a greater or less extent whenever solutions of two ionogens are mixed. In the latter case:

- (1) Two salts give two salts (pp. 380–382).
- (2) An acid and salt give a salt and an acid (p. 397).
- (3) A base and salt give a salt and a base (p. 398).
- (4) An acid and base give water and a salt (neutralization).

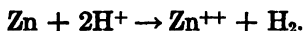
(1) is complete only when at least one product is insoluble. (2) and (3) are complete when at least one product is little ionized or

insoluble or both. (4) is almost always complete because water is generally less ionized than any other substance in the system.

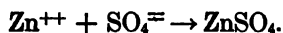
**2. Displacement of One Ion: Electromotive Series of the Metals.** — The displacement of hydrogen from dilute acids by metals (p. 118) now appears in a new light. These interactions do not occur in the absence of water (p. 119). The action will be formulated thus:



The sulphate-ion  $\text{SO}_4^-$ , although zinc sulphate is somewhat less ionized than sulphuric acid, is not much affected by the change and may be omitted:



Thus, this action, which takes place in the same fashion with most acids, concerns in reality only the hydrogen-ion in the solution, and is independent of the nature of the negative ion. True, hydrogen-ion cannot be used alone, for it is always accompanied by *some* negative radical. But the latter, like the vessel in which the experiment is made, is part of the necessary apparatus, and not an interacting substance. The action consists simply in the transference of the electric charges from the hydrogen to the zinc, whereby the latter becomes ionic. The discharged hydrogen is liberated as gas. The speed of the action, for any one metal, depends on the concentration of the hydrogen-ion, *i.e.*, on the activity of the acid. Hence the action goes faster with hydrochloric acid than with acetic acid. When the solution is evaporated, the ionogen, in the above case zinc sulphate, is formed:

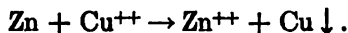


Similarly, fluorine displaces chlorine from chloride-ion (p. 281), chlorine displaces bromine from bromide-ion (p. 273):



and bromine displaces iodine from iodide-ion (p. 279). Each of these actions is independent of the nature of the other ion which accompanies the one undergoing change.

The same sort of displacement occurs with all positive ions. Thus, zinc will not only displace hydrogen, but also other metallic elements, like lead, copper, and silver, from the ionic condition in solutions of their salts:



Here the copper appears as a red precipitate. Lead, in turn, will displace copper and silver, but not zinc. Copper will displace silver. Thus the metals can be set down in an order such that each metal displaces those following it in the list and is displaced by those preceding it. This list (see below) is known as the **electromotive series** of the metals, because in electrolysis of normal solutions of their salts, the electromotive force of the current required to deposit

ELECTROMOTIVE  
SERIES OF THE  
METALS.

Alkali metals (*q.v.*)  
Alkaline earth  
metals (*q.v.*)  
Magnesium  
Aluminium  
Manganese  
Zinc  
Chromium  
Cadmium  
Iron  
Cobalt  
Nickel  
Tin  
Lead  
**Hydrogen**  
Copper  
Arsenic  
Bismuth  
Antimony  
Mercury  
Silver  
Palladium  
Platinum  
Gold

each metal (*cf.* p. 359) is less than that for the metal preceding in the list (see Chap. XXXVIII).

This list embodies many facts in the behavior of the metals, and should be **kept in mind as furnishing a key to the actions in which a free metal is used or produced.** For example, the chemical activity (p. 129) of the free metals places them in the same order. The earliest ones rust much more readily in air than do the later ones, provided the oxide does not adhere so firmly to the surface of the metal (*e.g.*, Al) as to protect it from further action of the oxygen in the air. Those following copper do not rust. Conversely, the oxides of the metals down to and including manganese, when heated in a stream of hydrogen, may give lower oxides, but are not completely reduced to the metallic condition. The oxides of cadmium and succeeding metals are easily reduced. The oxides of mercury and the last four metals are decomposed by heating alone. The relations of the metals in respect to combination with elements other than oxygen are similarly expressed by the arrangement in this table.

The position of hydrogen is particularly significant. It will be noted that none of the metals preceding hydrogen are found free in nature as ordinary minerals,\* while all of the metals succeeding hydrogen, although occurring to some extent in combination, are found also free. The explanation of this is that, by prolonged action upon ordinary water, containing, as it must, carbonic acid and other sources of hydrogen ions, the metals preceding hydrogen must

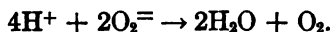
\* Free lead and tin do occur as rare minerals. Iron, with a little cobalt and nickel, constitutes many meteoric masses.

eventually displace the hydrogen-ion and pass into some form of combination (*cf.* p. 403). The metals following hydrogen do not displace hydrogen-ion and are much less affected by the agencies which are most active in the chemical transformation of minerals. Hence they often remain in the free state. For this reason gold, silver, and copper were the metals first used by man. Iron came into service much later.

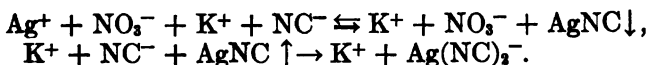
To avoid a common misconception, it must be noted that the electromotive series has no bearing on the tendency of one radical to dislodge another in *double decompositions*. The place of an element in the E.M. series defines its relative activity *when free*, and has to do only with actions where *one free element displaces* (p. 129) *another*. The influences which determine a double decomposition (*cf.* pp. 208, 382-384) are such as the insolubility of a compound, and have little to do with the chemical activity of the compounds concerned (p. 304) and nothing whatever to do with that of the free elements, for these, in fact, are not present at all. Thus, when silver chloride (insoluble) is placed in a solution of potassium iodide KI, it is quickly converted into silver iodide AgI. This happens because silver iodide is still more insoluble than is silver chloride. But free chlorine (the gas) will quickly displace the iodine from silver iodide.

The negative ions can be arranged in order in a similar way.

**3. Destruction or Formation of a Compound Ion.** — The destruction of a compound ionic material is observed in the action of any reducing agent, such as hydrogen peroxide (p. 320), upon a dilute solution of a permanganate. The compound ion  $\text{MnO}_4^-$  gives by reduction  $\text{Mn}^{++}$  and water. It also occurs when charcoal is added to hydrogen peroxide solution (p. 318), for the ion  $\text{O}_2^-$  of the peroxide gives the ion  $\text{O}^-$  (or  $\text{OH}^-$ ) of water and free oxygen:



The converse occurs when potassium cyanide is added in excess to a solution of a salt of silver. First, silver cyanide is precipitated, and then this compound unites with the excess of cyanide-ion:



The product is the soluble potassium argenticyanide. It is a salt of the *complex acid*  $\text{HAg}(\text{CN})_2$ , and not a double salt (p. 402). It does *not* decompose into potassium and silver cyanides and their ions when in solution, for the second action, above, is not appreciably reversible.

Actions of this class often proceed slowly, so that their speed can be measured.

**4. Change in the Charges of Two Ions.** — A decrease in the charge in two ions probably occurs in the preparation of chlorine (p. 219). The decomposition of the manganese tetrachloride takes place by the simultaneous discharge of two equivalents of electricity from the quadrivalent manganese ion and two chloride ions:



Both this sort of change and its converse are common with ions of metals such as iron and tin (*q.v.*), which have more than one valence.

**5. Charge and Discharge of Two Ions, Electrically.** — Discharge of ions is brought about in every electrolysis (p. 216). Thus, when hydrochloric acid is decomposed by the current, we have:



The converse takes place when the polarization current (p. 360) is allowed to flow. Both charge and discharge occur in every simple battery, as when zinc dissolves in dilute sulphuric acid to give zinc sulphate (pp. 29–30):



The creation of the positive charges on the zinc-ion in the former of the two equations leaves the rod of zinc negatively charged. The liberation of the positive charges from the hydrogen ions in the latter renders the platinum wire positive.

#### NON-IONIC MODES OF FORMING IONOGENS

While ionogens may always be made by the union of the proper ions, they must nevertheless, in the absence of the solvent, be regarded as chemical substances which may be constructed, and very frequently are made, out of their constituents without reference to the ionic plane of cleavage. Thus we have incidentally observed many ways in which acids, bases, and salts may be prepared that do not involve a union of the constituent ions and are not ionic.

**Acids and Bases.** — Oxygen acids can almost all be prepared from the **anhydride**, that is, from the oxide of the non-metal, which is not an ionogen, and water. Phosphoric acid, sulphurous acid (p. 149), and many other acids are so formed. The hydrogen halides are all producible by union of the constituent elements. Many acids are formed from others when the latter are heated; for example,

hydrochloric acid from hypochlorous acid (p. 223), chloric acid from hypochlorous acid (*q.v.*), and phosphoric from phosphorous acid (*q.v.*).

Bases are formed by the union of oxides of metals with water (p. 149).

**Salts.** — The dry ways of forming salts are very numerous. Thus, many are formed by direct union of the elements, as in the case of chlorides (p. 221), sulphides (p. 16), and other simple salts. Many are made by reduction or oxidation from other salts, as potassium chloride from potassium chlorate (p. 83), or potassium perchlorate (*q.v.*) from the latter. Often a reducing or an oxidizing agent is used, as in making sodium nitrite (*q.v.*) from the nitrate, and lead sulphate from lead sulphide (*q.v.*), no solvent being present. Almost all oxygen salts can be obtained by the union of two oxides, as calcium carbonate (*q.v.*) from calcium oxide and carbon dioxide. Ammonium salts are formed by combination of ammonia, which is not an ionogen, with anhydrous acids (p. 212).

**In manufacturing salts, non-ionic methods**, like the above, as well as those involving ionic actions, **are very commonly used**. In each case the cheapest and most easily accessible materials are chosen, and the least expensive operation is selected.

Neutralization is theoretically the simplest ionic way of getting a salt, because the water can be removed by mere evaporation. Yet most of the salts which are on the market are made by the use of other actions. In fact, the pure bases and acids are usually too expensive to be utilized as sources of salts.

The commonest definition of a salt, as a substance formed by the neutralization of an acid by a base, is open to many objections. It is logically defective because it does not describe what a salt is, but one method of making a salt, which is an entirely different matter. It is unfortunate in its choice amongst possible paralogisms, because neutralization is more significant as a method of forming water than as a means of preparing a salt. And finally, as we have just seen, the definition has not even the excuse of practical value, for most salts are manufactured by entirely different reactions.

**Exercises.** — 1. Using the data in regard to ionization (p. 367), formulate other dissociations according to the models on p. 377.

2. In the case of the green solution of cupric bromide (p. 379), explain in detail (p. 359) the effect of the addition of potassium bromide. Formulate the action (p. 380).

3. Give a list of all the colorless ionic substances you can think of (p. 375).

4. Formulate fully, according to the diagram on p. 382, the precipitation of barium sulphate (p. 385), of silicic acid from sodium silicate (p. 394), of zinc hydroxide from zinc sulphate (p. 396), of silver chloride from silver sulphate, and the liberation of hydrogen chloride by phosphoric acid (p. 207).

5. Give a list of the specific physical and chemical properties (p. 384) of iodide-ion, sulphate-ion, cupric-ion, chloride-ion.

6. Formulate (p. 403) the displacement of iodine by bromine (p. 279), and of bromine by chlorine (p. 273).

7. Explain the acid reaction of ferric chloride  $\text{FeCl}_3$  solution (p. 399).

8. Name all the physical components in aqueous solutions of potassium hydroxide, hydrogen chloride, and sulphuric acid (*cf.* p. 400).

9. Name the anions and cations whose formulæ are used on p. 375.

10. Formulate (p. 403) the actions of iron and of aluminium on dilute hydrochloric acid.

11. What is the molar concentration (p. 183) of hydrogen-ion in  $N/10$  hydrogen sulphide (p. 367) and in  $N/10$  acetic acid, of sodium-ion in  $N/2$  sodium chloride, and of cupric-ion in  $N$  cupric nitrate?

12. Combining the models on pp. 396 and 387, formulate the action of hydrochloric acid on magnesium hydroxide and on zinc hydroxide.

13. Formulate (p. 381) and discuss the action of sulphuric acid upon potassium permanganate (p. 320).

14. Formulate (p. 387) the neutralizations on pp. 396-397.

15. What do we infer (p. 401) from the fact that the solution of sodium hydrogen sulphide  $\text{NaHS}$  is neutral?

16. Invent an interaction of two soluble salts in which both products shall be insoluble (see Table of Solubilities, inside front cover).

17. To which classes of ionic actions do those of iodine on hydrogen sulphide (p. 278), and of magnesium on cold water (p. 115), belong? Formulate the former according to the model on p. 403.

18. What metals, beside platinum, would be most likely to form suitable electrodes for an electrolytic cell (p. 404)?

19. How should you attempt to obtain (p. 405) a pure aqueous solution of the acid  $\text{HAg}(\text{CN})_2$ ?

20. Formulate (p. 406) the electrolysis of hydriodic acid and that of cupric sulphate, the latter between copper electrodes (p. 360).

21. Give, for each of the following, two definitions, one in terms of

experimental facts, the other in terms of the ions: acid, base, salt, neutralization, acid salt, mixed salt.

22. Using the table of fractions ionized (p. 367), prepare lists of the pairs of ionic substances which show the greatest, and the least tendency to combine, and state in each case the proportion combining in decinormal solution.

23. In the case of the chocolate-brown, concentrated solution of cupric bromide (p. 378), explain in detail what would happen to the system: (a) if metallic zinc were to be added (p. 404); (b) if hydrogen sulphide gas were to be led into the solution ( $\text{CuS}$  is insoluble). Formulate each case.

24. What is implied by the statements, that peroxides are salts and that hydrogen peroxide is feebly acid (p. 393)?

25. Formulate after the model on p. 398, and discuss fully, the interaction of: (a) sodium peroxide and hydrochloric acid (p. 315); (b) barium peroxide and sulphuric acid.

26. For the neutralization of 77 c.c. of a certain alkaline solution, 25 c.c. of normal hydrochloric acid are required. What is the normal concentration of the alkali? If the alkali was sodium hydroxide, what weight of the substance was present? If the alkali was barium hydroxide, what weight of it was present?

27. What would be the behavior in a conductivity trough (Fig. 106) experiment, in which the layers were: (a) hydrochloric acid and sodium acetate in equivalent amounts, before and after mixing; (b) hydrochloric acid and sodium peroxide? Formulate both (p. 387) actions.



## CHAPTER XX

### SULPHUR AND HYDROGEN SULPHIDE

**Occurrence.** — Free sulphur is found in volcanic regions in Sicily, where it is mixed with gypsum and other minerals and occupies the pores of pumice-stone. Rocky materials accompanying a mineral in this way are called the **matrix**. The other important deposits are in Louisiana and in Texas (Brazoria county). There are many minerals, compounds containing sulphur, which are chiefly important on account of their other constituents. Sulphides of metals, such as pyrite  $\text{FeS}_2$ , copper pyrites  $\text{CuFeS}_2$ , galena  $\text{PbS}$ , zinc-blende  $\text{ZnS}$ , and sulphates, like gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , barite  $\text{BaSO}_4$ , and celestite  $\text{SrSO}_4$ , are fairly plentiful. The deposits of free sulphur are believed to have been formed mainly from gypsum, by reduction. Sulphur is a constituent of the proteins, which are important components of the structures of plants and of animals.

**Manufacture.** — In Sicily sulphur is obtained by the simple process of melting it away from the accompanying volcanic rock at a low temperature. A part of the sulphur itself is burned, to obtain heat to melt the rest, because no coal is found in Italy, and fuels other than sulphur are locally too expensive. The liquid sulphur is allowed to run into wooden molds, in which it solidifies in the form of **roll sulphur**, or **roll brimstone**. For many purposes this sulphur is sufficiently pure. To produce the best quality it is subjected to distillation from earthenware retorts. The vapor passes into a large brick chamber and condenses upon the walls and floor in the form of a fine powder, sold as **flowers of sulphur**. When the chamber has become heated, the sulphur condenses in the form of a liquid, which is drawn off and cast in molds as before.

In Louisiana, the sulphur forms a deposit over half a mile in diameter, below 900 feet of clay, quicksand, and rock. It is extracted by the Frasch method, by means of borings which permit four pipes, one within the other, to reach the deposit. Water, previously heated, under pressure to  $170^\circ$ , is pumped down the two outside pipes (6 and 8 inches in diameter). After time has been allowed for the melting

of a mass of the sulphur (m.-p.  $114.5^{\circ}$ ), compressed air is forced down the innermost, one-inch pipe. The melted sulphur has twice the specific gravity of the water in the outer pipes. But the mixture of air and sulphur has about the same specific gravity, and so flows freely up the three-inch pipe surrounding the air pipe. The element flows into a large, wooden enclosure, in which it solidifies, and is practically pure sulphur. Each well, until obstructed by collapse of the rock and quicksand at the bottom, produces 500 tons a day.

The greater part of the sulphur of commerce formerly came from Sicily, where, in 1898, 447,000 tons were manufactured against 41,000 tons elsewhere. The whole supply of the United States (250,000 tons) is now obtained from Louisiana and Texas. In 1913, Sicily produced 407,307 tons and Japan 58,452 tons, and in 1914 an island off the coast of New Zealand furnished 12,000 tons. The world's consumption is over 800,000 tons.

Some sulphur is also obtained from the exhausted material used in removing sulphur from illuminating-gas during its purification.

**Physical Properties.**—The chief physical peculiarity of sulphur is that, instead of existing in three familiar physical states only, like water, it possesses two familiar and perfectly distinct solid forms and two different liquid states of aggregation.

1. **Rhombic Sulphur.** Native sulphur is yellow, has a sp. gr. 2.06 and melts at  $112.8^{\circ}$ . It is almost insoluble in water, but dissolves freely in carbon disulphide (41 parts in 100 at  $18^{\circ}$ ) and in sulphur monochloride (*q.v.*). The crystals of native sulphur, as also those obtained by evaporating a solution, belong to the rhombic system (Fig. 8, p. 14). Roll sulphur, and most specimens of flowers of sulphur, are the same substance, although the crystals in their growth have interfered with one another, and the mass is **crystalline**, simply, and not **well crystallized**. This variety is called, from its form, **rhombic sulphur**. This form is stable below  $96^{\circ}$ . Above that temperature it changes slowly into monoclinic sulphur.

2. **Monoclinic Sulphur.** When a large mass of melted sulphur solidifies slowly, and the crust is pierced and the remaining liquid poured out before the whole has become solid, the interior is found to be lined with long, transparent needles (Fig. 109). This kind of sulphur is nearly colorless, has a sp. gr. 1.96, melts at  $119.25^{\circ}$ , and is in all physical respects a different individual from



FIG. 109.

rhombic sulphur. This variety is named, from the system to which its crystals belong, **monoclinic sulphur**.

Monoclinic sulphur can be kept only *above*  $96^{\circ}$  and below its melting-point ( $119.25^{\circ}$ ). Every recently solidified mass of sulphur is composed of it. But, below  $96^{\circ}$  the mass gradually becomes opaque, the change usually spreading from the points at which it has been touched and finally affecting the whole mass. The opacity is due to the fact that the material has turned into an aggregate of small particles of rhombic sulphur, each of which occupies less space than the monoclinic sulphur from which it was formed. Conversely, rhombic sulphur, when heated *above*  $96^{\circ}$ , but not as high as its melting-point, turns slowly into monoclinic sulphur. Contact with a piece of monoclinic sulphur, or mere rubbing with a hard body, will determine the point at which the transformation shall begin, and the expansion which accompanies this results in a spreading opacity as before. The delay before the change starts and the effect of rubbing and inoculation are familiar in connection with almost all changes of state (*cf.* p. 194).

Transitions, marked by definite points, like this one at  $96^{\circ}$ , are attended by similar phenomena, whether they lie between two solid states, or a liquid and a solid state (ice and water), or a gaseous and a liquid state (steam and water). Heat is given out when we pass in one direction and absorbed by passage in the other. The rate of change of vapor pressure with change in temperature (*cf.* p. 200) is different on each side of the transition point. A body which has two solid states, and, therefore, two crystalline *forms*, is said to be **dimorphous** (two-formed), and one with more than two such states **polymorphous** (see Ammonium nitrate). But this term is not intended to imply that the relation of two solid states to each other is essentially different from that of two states of different kinds, such as solid and liquid, although the term "polymorphous" is not applied to the latter.

3.  $S_{\lambda}$  and  $S_{\mu}$ ; Vapor. When melted sulphur is heated, it undergoes a gradual change, which is especially noticeable near  $160^{\circ}$ . The formerly **pale-yellow, mobile liquid** ( $S_{\lambda}$ ) suddenly becomes **dark-brown** in color (color chiefly due to organic impurities) and so **viscous** ( $S_{\mu}$ ) that the vessel may be inverted without loss of material:  $S_{\lambda} \rightleftharpoons S_{\mu}$ . The liquid is a mixture, containing increasing proportions of  $S_{\mu}$ , namely, at  $120^{\circ}$  3.6 per cent, at  $160^{\circ}$  11 per cent, and at  $444.7^{\circ}$  over 30 per cent. Beyond  $260^{\circ}$  the viscosity becomes less, and at  $444.7^{\circ}$  the liquid boils and passes into sulphur vapor.

**Insoluble, Amorphous Sulphur  $S_{\mu}$ .** — When sulphur which has been exposed to the air is boiled and then allowed *slowly* to cool, the product is crystalline and soluble in carbon disulphide, as before. But when such impure sulphur is boiled and then *suddenly chilled* by pouring into cold water, it is at first semi-fluid. After several days this *plastic sulphur*, as it is called, becomes hard. It is then found to contain rhombic sulphur mixed with about 34 per cent of another variety of free sulphur, namely,  $S_{\mu}$ . This variety is almost insoluble in any solvent, and so may be secured by washing the mixture with carbon disulphide.

This **insoluble sulphur**, being without crystalline structure, is called also **amorphous** (Gk. & priv., *μορφή* form) sulphur. Now amorphous bodies (see Glass) are always supercooled liquids, that is, liquids still existing as such at a temperature at which the solid, crystalline form is the stable one. They have been brought, by cooling, so rapidly through their freezing-point, that crystallization has not had time to begin (*cf.* p. 175) and a general rigidity only has supervened. Now amorphous sulphur is viscous, liquid sulphur  $S_{\mu}$  which, by sudden chilling, has been carried past both the gradual transition to mobile liquid sulphur  $S_{\lambda}$ , and the crystallization as well, without undergoing either of these changes. It is supercooled  $S_{\mu}$ . This accounts for the fact that it is obtainable only by rapid cooling. Once the mixture has been obtained by chilling, the insoluble sulphur reverts very slowly to the soluble variety, and years are required for the completion of the reversion at room temperature. At 100° the reversion is completed in an hour.

The capacity of the  $S_{\mu}$  to be supercooled at all seems to depend on the presence of traces of foreign bodies. Of these, iodine is the most efficient. The sulphuric acid, produced by prolonged exposure of the sulphur to the air (see below), is the agent usually responsible for the supercooling. Freshly recrystallized sulphur gives no plastic sulphur and no insoluble sulphur. Destruction of the trace of free acid, by leading ammonia gas through the boiling sulphur, likewise gives a liquid which, when chilled, yields nothing but crystalline sulphur [*Lect. exp.*]. Iodine and sulphuric acid are negative catalysts.

Insoluble sulphur is sometimes found in flowers of sulphur and always in sulphur formed by precipitation from thiosulphates (*q.v.*) in presence of acids.

**Chemical Properties.** — When the density of sulphur vapor is determined at low temperatures and under reduced pressures, the

molecular weight corresponds closely to the formula  $S_8$ . As the temperature is raised, however, the vapor expands very rapidly, and at  $800^\circ$  the molecular weight is 64.2, and the formula therefore  $S_8$ . Intermediately, mixtures of  $S_8$ ,  $S_6$ , and  $S_2$  exist (Preuner and Schupp). The formula of dissolved sulphur, as measured by freezing- and boiling-point methods (p. 335), is  $S_8$ .

We do not ordinarily think of sulphur as a very active chemical substance, but this is largely due to the fact that its solid condition interferes with the attainment of close contact with the body upon which it acts. It is really very active. When finely divided *metals*, with the exception of gold and platinum (*cf.* p. 404), are rubbed together with powdered sulphur, union takes place and sulphides are produced. Sulphur, when heated, combines with great vigor with iron (p. 16), copper, and most of the metals. Sulphur unites also with many of the *non-metals*. Thus with oxygen it produces sulphur dioxide (p. 88), and even sulphur trioxide  $SO_3$ . It unites also with chlorine directly. When sulphur is treated with oxidizing agents *in presence of water*, no trace of sulphur dioxide (or sulphurous acid) is formed; the only product is sulphuric acid (see p. 446). Even the oxygen in the air slowly oxidizes sulphur, with the help of atmospheric moisture, to give sulphuric acid,  $2S + 2H_2O + 3O_2 \rightarrow 2H_2SO_4$ .\*

**Uses of Sulphur.** — Large quantities of crude sulphur are employed for making sulphur dioxide, which is used in the manufacture of sulphuric acid, in bleaching feathers, straw, and wool, in preparing dried fruits, and in making alkali sulphites for employment in the bleaching industry and in paper-making. The manufacture of carbon disulphide consumes much sulphur. Purified sulphur is employed in the manufacture of gunpowder, fireworks, matches and, by combination with rubber, of vulcanite. Flowers of sulphur is used in vineyards to destroy fungi, which it does by virtue of the traces of sulphuric acid it yields by oxidation.

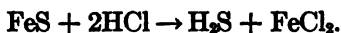
### HYDROGEN SULPHIDE $H_2S$ .

This compound is found in some mineral waters, which in consequence are known as sulphur waters. It is produced in the decomposition of animal matter containing sulphur (proteins), when air is excluded, and the odor of rotten eggs is due in part to its presence.

\* The paragraph on the chemical relations of the element (see end of this chapter) should be read at this point.

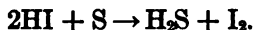
**Preparation.** — 1. Hydrogen and sulphur do not unite perceptibly in the cold. At  $310^{\circ}$  almost complete union occurs, but about 168 hours (7 days) are required for the change.

2. Sulphides of metals, being salts, are acted upon more or less easily by dilute acids (p. 397), and give hydrogen sulphide. Ferrous sulphide, the least expensive of those easily affected, is generally used:

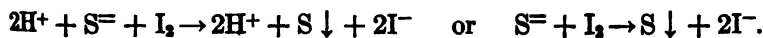


For hydrochloric acid we may substitute an aqueous solution of any active, *non-oxidizing* acid (see p. 416). A Kipp's apparatus (p. 119) is commonly employed. The theory of this action is discussed later (see p. 419).

3. Hydrogen sulphide is the invariable product of the extreme reduction of any sulphur compound. Thus, it is formed by the action of hydrogen iodide upon concentrated sulphuric acid (p. 277). Even sulphur itself is reduced by *dry, gaseous* hydrogen iodide:



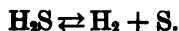
The action appears to be just the reverse of that which takes place in aqueous solution (p. 278), but in reality is quite different. Iodine and gaseous hydrogen sulphide will not produce free sulphur and gaseous hydrogen iodide, for this action would involve a considerable increase in energy in the system. But, in water, they do give hydrogen-ion and iodide-ion, for these bodies contain very much less energy than does hydrogen iodide:



This action is simply an ionic displacement.

**Physical Properties.** — Hydrogen sulphide is a colorless gas with a characteristic odor. When liquefied, it boils at  $-62^{\circ}$ , and in solid form melts at  $-83^{\circ}$ . At  $12^{\circ}$  the liquid exerts a pressure of 15 atmospheres. The solubility in water at  $10^{\circ}$  is 360 volumes in 100, and becomes less as the temperature is raised. The gas can be driven out completely by boiling the solution (*cf.* p. 211). The gas is very poisonous, one part in two hundred being fatal to mammals, and more than once fatal accidents have occurred in chemical laboratories.

**Chemical Properties of the Gas.** — When heated, the gas dissociates, and is therefore not very stable:



At  $310^{\circ}$  the decomposition, although very slow, affects a small but perceptible proportion of the gas before coming to rest. The dissociation, like most thermal dissociations, is accompanied by an absorption of heat and is therefore greater at higher temperatures (*cf.* p. 305).

The gas burns in air, forming steam and sulphur dioxide. The temperature of the mantle of flame surrounding the gas, as it issues from a jet, being far above  $310^{\circ}$ , the gas in the interior is dissociated before it meets with any oxygen. Hence a cold dish held across the flame (Fig. 110) receives a deposit of free sulphur, and a part of the hydrogen is also liable to escape unburnt. It may be remarked that the dissociation of this kind probably precedes the combustion of most gaseous compounds (see Flame).

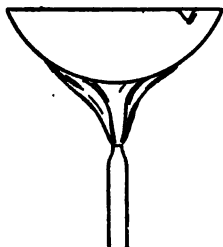
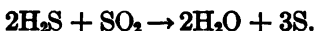


Fig. 110.

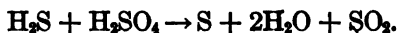
The metals, down to and including silver in the electromotive series, when exposed to the gas, quickly receive a coating of sulphide. The tarnishing of silver in the household is probably due to a trace of hydrogen sulphide in the illuminating gas which escapes from slight leaks in the pipes. The gas should thus behave like free sulphur shows its instability.

This instability is shown also in the fact that its hydrogen reduces substances, such as sulphur dioxide, which are not affected by free hydrogen:



This action takes place much more rapidly when the gases are moist than when they are dry (p. 97), and is retarded by dilution with indifferent gases (*cf.* p. 291). Native sulphur is occasionally produced by this action (see, however, p. 410, par. 1), as both of these gases are found issuing from the ground in volcanic neighborhoods. Sulphur is deposited also when hydrogen sulphide undergoes a partial combustion with a restricted supply of oxygen:  $2\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{S}$ .

When hydrogen sulphide gas is led through concentrated, or even, simply, normal sulphuric acid, the acid is reduced, sulphur dioxide escapes, and sulphur is deposited:



The sulphuric acid may be written  $\text{H}_2\text{O}, \text{SO}_3$ . In furnishing  $\text{SO}_2$ , therefore, each molecule can give one unit of oxygen and therefore

oxidize one molecule of  $\text{H}_2\text{S}$  (see p. 426). On account of this action the gas cannot be dried by means of concentrated sulphuric acid. Calcium chloride is likewise inapplicable, since a partial interchange takes place, resulting in the production of calcium sulphide and hydrogen chloride gas. Only a dehydrating agent, such as phosphoric anhydride, with which it cannot interact, is suitable for drying the gas.

**A Characteristic of Reduction and Oxidation.** — In the first of the three actions last mentioned, it will be seen that, while the  $\text{SO}_2$  was reduced to S, at the same time  $\text{H}_2\text{S}$  was oxidized (to S). In the second action,  $\text{H}_2\text{S}$  was oxidized to S, and  $\text{O}_2$  was reduced to  $2\text{H}_2\text{O}$ . In the last action,  $\text{H}_2\text{S}$  was oxidized to S, and  $\text{H}_2\text{SO}_4$  was reduced to  $\text{SO}_2$ . It is a characteristic of such actions that one substance is oxidized and another reduced: oxidation and reduction always occur together, in the same reaction. Here, under hydrogen sulphide, we speak of its *reducing* effect on sulphur dioxide, or on sulphuric acid. Under sulphur dioxide and sulphuric acid, however, we should speak of the oxidizing effect of the substance on hydrogen sulphide.

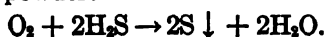
**Chemical Properties of the Aqueous Solution of Hydrogen Sulphide.** — While the gas itself is not an acid, its solution in water gives a feeble acid reaction with litmus, and is sometimes named **hydrosulphuric acid**  $\text{H}_2\text{S}$ , Aq. The conductivity of a  $N/10$  aqueous solution is small, and only 0.0007 (0.07 per cent) of the substance is ionized:



Some  $\text{S}^{=}$  ions are present. But hydrosulphide-ion  $\text{HS}^-$ , although an acid, is less dissociated than is water itself, and the amount of sulphide-ion is therefore very small. The salts of hydrosulphide-ion, such as  $\text{NaHS}$  (sodium acid sulphide, see next section), give therefore neutral solutions. This behavior is the rule with the acid salts of feeble dibasic acids (p. 401).

As an acid, the solution of hydrogen sulphide may be neutralized by bases. For the same reason it enters into double decomposition with salts (see next section).

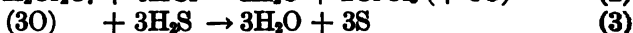
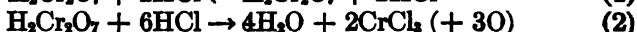
By the action of **oxygen** from the air upon an aqueous solution of hydrogen sulphide, the **sulphur** is slowly **displaced** and appears in the form of a fine white powder:





This is an action similar to the displacement of ionic iodine by free chlorine (p. 279). On the other hand, the hydrogen may be displaced by metals, particularly the more active ones, but the small degree of ionization makes the action very slow.

The solution of the gas is a **reducing agent**, as its action upon iodine shows (p. 278). So, also, in presence of an acid, it removes oxygen from dichromic acid, produced by the action of an acid upon potassium dichromate:



Adding:  $\text{K}_2\text{Cr}_2\text{O}_7 + 8\text{HCl} + 3\text{H}_2\text{S} \rightarrow 2\text{KCl} + 2\text{CrCl}_3 + 7\text{H}_2\text{O} + 3\text{S}$

The first partial equation (cf. p. 269) represents the regular interaction of two ionogens, but the second interaction does not take place unless an oxidizable body (here the hydrogen sulphide) is present to take possession of the oxygen which it is capable of delivering (cf. p. 320). This action illustrates the decomposition of a compound ion (p. 405). Here  $\text{Cr}_2\text{O}_7^{=}$  gives chromic-ion  $\text{Cr}^{+++}$  and water.

**Sulphides.** — As a di-basic acid (p. 372), hydrogen sulphide gives both acid and normal (or neutral) sulphides, such as  $\text{NaHS}$  and  $\text{Na}_2\text{S}$ .

The acid sulphides are obtained by passing the gas *in excess* into solutions of soluble bases:

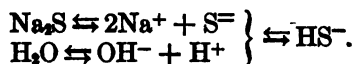


and are *neutral* in reaction. Their negative ion,  $\text{HS}^-$ , gives practically no hydrogen-ion (see preceding section).\*

By adding to the above solution an amount of sodium hydroxide equal to that used before, and driving off the water by evaporation, the second unit of hydrogen is displaced, and normal ("neutral") sodium sulphide, in solid form, is obtained:

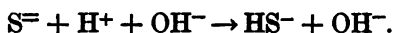


This action is wholly reversed when dry sodium sulphide is dissolved in water, the salt being completely hydrolyzed to the acid salt:



\* In point of fact, *N*/10 sodium-hydrogen sulphide, at 25°, is slightly hydrolysed (0.14 per cent, James Walker), and gives therefore a faint alkaline reaction.

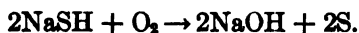
The  $\text{HS}^-$  gives a lower concentration of hydrogen-ion than does the water, and hence uses up in its formation the ions of hydrogen produced by the latter until an amount of hydroxyl equivalent to half the sodium is formed. The abbreviated equation shows this more clearly:



The solution is therefore strongly alkaline in reaction. In general, normal salt derived from an active base and a weak acid is hydrolysed to some extent by water and gives an alkaline solution.

In the abbreviated formulation used above, the union of  $\text{Na}^+$  and  $\text{OH}^-$  to form  $\text{NaOH}$  is not shown, because it is slight in dilute solution and does not affect the result. The union of  $\text{S}^{=2}$  and  $\text{H}^+$  to form  $\text{HS}^-$  is alone shown, because it is extensive and significant. To save space, this plan will be used in future, where the same situation exists.

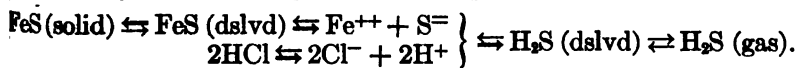
The soluble acid sulphides are oxidized in aqueous solution by atmospheric oxygen:



The sulphur is not precipitated, but combines with the excess of the sulphide, forming polysulphides (see below). Some sodium thiosulphate is produced at the same time.

**The Action of Acids on Insoluble Sulphides.**—The interaction of sulphides and acids is itself so important a matter in chemistry, and is so similar in theory to many other kinds of actions, that special attention should be given to it. The common method of preparing hydrogen sulphide from ferrous sulphide affords a suitable illustration.

Since ferrous sulphide is but slightly soluble in water, the action proceeds by a rather complex series of equilibria:



It will be seen that a number of reversible changes are involved, and the question is: Why does the reaction proceed forward, as it does? To answer this question, a consideration of each of the equilibria, separately, is required.

1. The dissolved hydrogen sulphide is very feebly ionized, and maintains a smaller concentration of sulphide-ion  $\text{S}^{=2}$  than does ferrous sulphide, in spite of the comparative insolubility of the

latter. Hence, the  $S^{=}$  formed from the  $FeS$  is continuously removed by union with the hydrogen-ion furnished by the acid,  $S^{=} + 2H^{+} \rightleftharpoons H_2S$ , and all the other equilibria are constantly displaced forward on this account. The action is therefore, in essence, like neutralization (p. 387).

It will be observed that the action takes place on account of the feeble ionization of the weak acid. We should therefore say that the weak acid *withdraws*, and not, as is sometimes done, that the strong acid *drives* it out.

Since the action is an ionic one, the acids must be employed in dilute form. This is true especially of oxygen acids. Thus, concentrated sulphuric acid has little action upon ferrous sulphide in the cold, and when the substances are heated the oxygen of the sulphuric acid comes into play, and sulphur dioxide (*q.v.*) and free sulphur are formed.

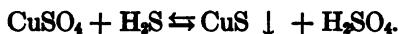
2. The union of  $S^{=}$  and  $2H^{+}$  depends on the magnitude of the *product* of their concentrations (p. 359),  $[S^{=}] \times [H^{+}] \times [H^{+}]$ , or  $[S^{=}] \times [H^{+}]^2$ . Hence, although  $[S^{=}]$  is minute, on account of the insolubility of  $FeS$ ,  $[H^{+}]$  is large on account of the great dissociation of the  $HCl$  and the fact that a strong solution of the acid can be used. Thus the *product* may be large enough for the purpose.

3. When a still less soluble sulphide, like cupric sulphide  $CuS$ , is employed, the concentration of the sulphide-ion  $[S^{=}]$  is too small to play its part and the action makes almost no progress. In this case, a concentration of  $H^{+}$ , sufficient to raise the product to the necessary value, cannot be obtained with any acid.

4. The fact that hydrogen sulphide is fairly soluble (3.6 vols. : 1 vol.) *hinders* the action. It prevents that free escape of one product which is so constantly a factor in promoting reversible chemical changes. Thus, if cadmium sulphide  $CdS$ , which lies between ferrous and cupric sulphides in solubility, is employed along with rather dilute hydrochloric acid, a concentration of hydrogen sulphide sufficient to stop the action accumulates before the liquid is saturated with the gas, and the latter can begin to escape. There are then two ways of making this action continuous. Either stronger hydrochloric acid, giving a higher concentration of  $H^{+}$ , may be used to force the formation of more  $H_2S$  (by union of  $2H^{+}$  and  $S^{=}$ ), or the reverse action, due to accumulation of  $H_2S$  (dissolved), may be diminished mechanically by leading air through the mixture (p. 189) and so removing the hydrogen sulphide as fast as it is formed. Either plan will cause complete interaction with the cadmium sulphide.

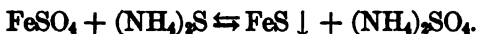
**Classification of Insoluble Sulphides.** — In analytical chemistry, advantage is taken of the different solubilities of the sulphides, for the purpose of identifying the metallic elements, and of separating mixtures containing several such elements. Three classes are distinguished.

1. The sulphides of silver, copper, mercury, and some other metals are exceedingly insoluble, and, therefore, do not interact with dilute acids as does ferrous sulphide (p. 420). These may therefore be made by leading hydrogen sulphide into solutions of their salts:



The acid produced has scarcely any effect upon the sulphide, and almost no reverse action is observed. In this action the sulphide-ion is the active substance and, by its removal, all the equilibria are displaced forward.

2. The sulphides of iron, zinc, and certain other metals are insoluble in water, but not so much so as the last class. Hence they are decomposed by dilute acids, and the reverse of the above action takes place almost completely. These sulphides must therefore be made, either by combination of the elements, or by adding a soluble sulphide to a solution of a salt:



No acid is produced in this sort of interaction, and the considerable insolubility of the sulphide of iron or zinc in water renders the change nearly complete. The solubility of cadmium sulphide (p. 420) places it between this group and the previous one.

3. The sulphides of barium, calcium, and some other metals (*q.v.*), although insoluble in water, are hydrolyzed by it, and give soluble products, the hydroxide and hydrosulphide:



They may be prepared by direct union of the elements, and from the sulphates by reduction with carbon. But they are not precipitated by hydrogen sulphide or ammonium sulphide.

**Polysulphides.** — When sulphur is shaken with a solution of a soluble sulphide or acid sulphide, such as sodium sulphide, it dissolves, and evaporation of the solution leaves residues, varying in composition from  $\text{Na}_2\text{S}_2$  to  $\text{Na}_2\text{S}_6$ . These appear to be mixtures composed mainly of  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{S}_4$ .

When an acid is poured into sodium polysulphide solution minute spherules of rhombic sulphur are precipitated:



This precipitate has been called "soluble amorphous sulphur." It is certainly all soluble in carbon disulphide, but the particles rotate the plane of polarization of polarized light (A. Smith), and are therefore crystals. Insoluble amorphous sulphur, in appreciable quantities, cannot be obtained under any conditions from polysulphides. It is obtained by adding sodium thiosulphate solution to concentrated, active acids.

When the order is reversed, sodium pentasulphide being thrown into concentrated hydrochloric acid, no hydrogen sulphide is evolved. **Hydrogen pentasulphide**,  $\text{H}_2\text{S}_5$ , a yellow oil, falls to the bottom of the vessel.

**The Chemical Relations of the Element.** — In combination with metals and hydrogen, sulphur is bivalent, forming compounds like  $\text{H}_2\text{S}$ ,  $\text{FeS}$ ,  $\text{CuS}$ , and  $\text{HgS}$ . In combination with non-metals, however, the valence is frequently greater, the maximum being seen in sulphur trioxide, where we must assume that the sulphur is sexivalent. Its oxides are acid-forming, and it is, therefore, a non-metal.

Sulphur is regarded as resembling oxygen more closely than any of the other elements *we have studied so far*. Both unite directly with most metals and non-metals. In this they are like chlorine. But hydrogen chloride is highly ionized by water, while the hydrogen compounds of oxygen and sulphur are feebly ionized. The formulæ of the compounds of oxygen and sulphur with metals are similar,  $\text{CuO}$  and  $\text{CuS}$ ,  $\text{NaOH}$  and  $\text{NaSH}$ , and so forth, but this is in part due merely to the fact that both elements are bivalent. The chemical resemblance of sulphur to selenium and tellurium (*q.v.*) is much more striking than its resemblance to oxygen.

**Exercises.** — 1. The freezing-point of pure sulphur is found to vary from  $119^\circ$  down to  $114^\circ$ , depending upon the temperature to which the liquid has been heated and the speed with which it has been cooled. To what should you attribute this variability?

2. How could the decomposition of hydrogen sulphide at  $310^\circ$  be rendered (a) more complete, (b) less complete? Would the percentage decomposed be affected (a) by reducing the pressure, (b) by mixing the gas with an indifferent gas?

3. What are the relative volumes of the gases (p. 259) in the action of, (a) hydrogen iodide and sulphur, (b) hydrogen sulphide and sulphur dioxide?

4. To what classes of ionic actions (p. 402) do the interactions of hydrogen sulphide solution and (a) oxygen (p. 417), (b) acidified potassium dichromate (p. 418), (c) sodium hydroxide (p. 418), (d) iodine (p. 278), belong?

5. Why is normal sodium sulphide only half hydrolyzed by water?

6. Formulate completely, after the model on p. 419, the actions of, (a) hydrogen sulphide and cupric sulphate solution; (b) ammonium sulphide and ferrous sulphate. In each case explain which equilibrium determines the direction of the action.

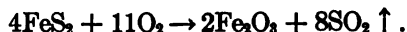
## CHAPTER XXI

### THE OXIDES AND OXYGEN ACIDS OF SULPHUR

FOUR oxides of sulphur, represented by the formulæ  $S_2O_3$ ,  $SO_2$ ,  $SO_3$ , and  $S_2O_7$ , are known. Of these, however, the first and the last are much less familiar substances than the other two. The dioxide and trioxide of sulphur are not only important in themselves, but their relation to the acids  $H_2SO_3$  and  $H_2SO_4$ , which may be obtained from them by the addition of water, makes them doubly so to the chemist.

*The Preparation of Sulphur Dioxide  $SO_2$ .*—1. When sulphur burns in air or oxygen, sulphur dioxide is produced (p. 88).

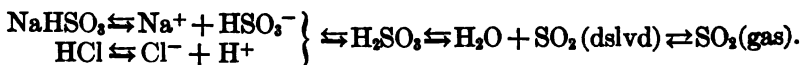
2. The larger part of the sulphur dioxide used in commerce is probably obtained by the **roasting (calcining)** of sulphur ores. Pyrite  $FeS_2$ , for example, which is a familiar yellow, metallic-looking mineral, can be burnt in a suitable furnace on account of the large amount of sulphur which it contains:



The gas, although mixed with a great amount of nitrogen which entered as part of the air, can be used to make sulphuric acid.

It should be noted, in passing, that heating and roasting or calcining are distinct processes in chemistry. **Roasting** or **calcining** always assumes the access of the air and employment of its oxygen; **heating**, in the absence of modifying words, assumes the exclusion or the chemical indifference of the air.

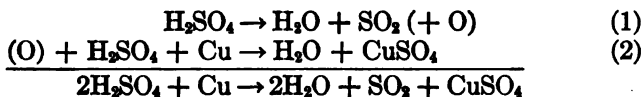
3. In the laboratory, a steady stream of gas is obtained by allowing hydrochloric acid to drop upon solid sodium acid sulphite, or concentrated sulphuric acid to trickle into a 40 per cent solution of the same salt (Fig. 41):



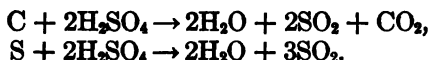
The sulphurous acid being only moderately ionized, its molecules are formed in considerable amount. Being also unstable, it decomposes

spontaneously into water and sulphur dioxide, and the latter escapes when sufficient water for its solution is not present.

4. Sulphur dioxide can also be made by the reduction of concentrated sulphuric acid by copper at a high temperature. Copper is the metal most commonly employed, because by its means very pure sulphur dioxide can be obtained. More active metals, such as iron and zinc, although cheaper, cannot be used, since they reduce the sulphuric acid to hydrogen sulphide. The undiluted hydrogen sulphate consists entirely of molecules and, at the high temperatures at which alone the action is vigorous, is an oxidizing agent (*cf.* p. 119). A part of the acid loses oxygen to form water with the hydrogen of another molecule:



Some easily oxidized non-metals, such as carbon and sulphur, act in the same way:



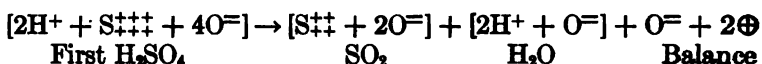
#### **Making Equations by Positive and Negative Valences.**—

Equations like the foregoing can be constructed also by assuming that each element in a compound is either positive or negative, and by marking the valences accordingly (for details, see p. 493). Thus, in sulphuric acid, we have  $2\text{H}^+$  (positive, univalent) and  $4\text{O}^-$  (each bivalent and negative). Since the numbers of positive and negative valences must be equal, and we have  $2\oplus^*$  and  $8\ominus$ , it follows that the sulphur carries  $6\oplus$ ,  $\text{S}^{++++}$ .

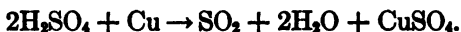
Now when, in making the experiment, we find the products  $\text{SO}_2$  and  $\text{CuSO}_4$ , we may infer that the hydrogen formed water. We infer, also, that to obtain *two* compounds containing sulphur, at least  $2\text{H}_2\text{SO}_4$  was required. We then note that the S in  $\text{SO}_2$  is quadrivalent. Hence  $\text{S}^{++++}$  became  $\text{S}^{++}$  and  $2\oplus$  were released. The metallic copper used was free and without valence, and became  $\text{CuSO}_4$ , in which it is  $\text{Cu}^{++}$ . It obtained the  $2\oplus$  from the sulphur. The action can therefore be analyzed as follows:

\* The signs  $\oplus$  and  $\ominus$  stand for quantities of electricity equal to those carried by one equivalent of an ionic substance, and therefore required for its discharge and liberation.





The second  $\text{H}_2\text{SO}_4$  gives  $[2\text{H}^+ + \text{SO}_4^-]$ . The Cu takes the  $2\oplus$  giving  $\text{Cu}^{++}$ , and this with the  $\text{SO}_4^-$  gives  $\text{CuSO}_4$ . The  $2\text{H}^+$  takes the  $\text{O}^-$  from the balance, giving  $\text{H}_2\text{O}$ . Thus, the whole balance is used and the products are accounted for. The equation must therefore be:



It will be noted that the two molecules of sulphuric acid play different rôles. Only one of them is used in oxidizing.

Similarly, with sulphuric acid and carbon, the same analyzed equation applies. The carbon gives  $\text{CO}_2$ . Thus, the carbon goes from  $\text{C}^0$  to  $\text{C}^{\text{++}}$ . To obtain the  $4\oplus$ ,  $2\text{H}_2\text{SO}_4$  is required (equation above). Hence,



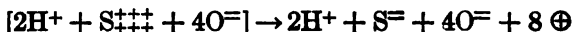
When hydrogen sulphide is led through concentrated sulphuric acid, the latter is reduced to sulphur dioxide, and the former is oxidized, giving free sulphur (p. 416):



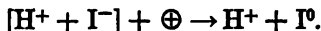
Since this action requires  $2\oplus$ , and sulphuric acid in giving  $\text{SO}_2$  delivers  $2\oplus$ , it follows that  $1\text{H}_2\text{SO}_4$  will decompose  $1\text{H}_2\text{S}$ :



Finally, when HI with sulphuric acid (p. 277) gives free iodine ( $\text{I}^0$ ), and  $\text{H}_2\text{S}$  ( $2\text{H}^+ + \text{S}^-$ ), evidently  $\text{S}^{\text{+++}}$  in sulphuric acid gives up  $8\oplus$ , becoming  $\text{S}^-$ :



and



Evidently,  $1\text{H}_2\text{SO}_4$  giving  $8\oplus$  will interact with  $8\text{HI}$ , changing  $8\text{I}^-$  into  $8\text{I}^0$ . Hence,



The reader should practice the use of this method by making the equations for the actions of zinc (p. 119) and of hydrogen bromide (p. 272) upon sulphuric acid.

**Physical Properties.**—Sulphur dioxide is a gas possessing a penetrating and characteristic *odor*. This is frequently spoken of as

the "odor of sulphur," but it should be remembered that sulphur itself has scarcely any smell at all. The weight of the G.M.V. of the gas (65.54 g.) shows it to be more than *twice as heavy as air*. The critical temperature is  $156^{\circ}$ . By means of a freezing mixture of ice and salt (Fig. 111), the gas is easily condensed in a U-tube to a transparent, mobile *fluid*, which boils at  $-8^{\circ}$ . At  $0^{\circ}$  the vapor tension of the liquid is 3.25 atmospheres, so that the liquid is handled and sold in glass syphons, or in sealed tin cans. The liquid may be frozen to a white solid, melting at  $-76^{\circ}$ . It ionizes substances dissolved in it as well as does water (cf. p. 357). The *solubility* of the gas in water, 5000 volumes in 100, is very great. Unlike solutions of the hydrogen halides (p. 211), however, the liquid is completely freed from the gas by boiling.

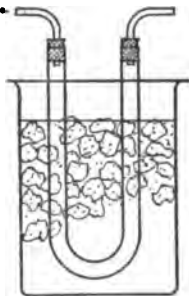


FIG. 111.

**Chemical Properties.** — Sulphur dioxide is **stable**, being decomposed only by the use of a very high temperature.

It **unites with water** to form sulphurous acid,  $\text{H}_2\text{SO}_3$ , which is unstable and exists only in solution. Although the gas itself sometimes receives this name, it is not acid: it is simply the anhydride (p. 150) of the acid. The only compound of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  that has been isolated is a solid hydrate  $\text{SO}_2 \cdot 7\text{H}_2\text{O}$ .

Since the maximum valence of sulphur is 6, sulphur dioxide, in which but four of the valences of sulphur are used, is **unsaturated**. It is therefore still able to combine directly with suitable elements, such as chlorine and oxygen. When it is mixed with chlorine in sunlight, a liquid, **sulphuryl chloride**  $\text{SO}_2\text{Cl}_2$ , is produced.

Liquefied sulphur dioxide is now sold in tin cans, and is employed for bleaching straw, wool, and silk. As a disinfectant it has been displaced to a large extent by formaldehyde.

**The Liquefiabilities of Gases.** — It will assist us in recalling which gases are hard to liquefy and which easy, if we memorize the fact that Faraday (from 1823 to 1845) liquefied most of the familiar gases and failed only with three, namely **hydrogen** (c.t.  $-242^{\circ}$ ), **oxygen** (c.t.  $-113^{\circ}$ ), and **nitrogen** (c.t.  $-146^{\circ}$ ). These, with **nitric oxide**  $\text{NO}$  (c.t.  $-93.5^{\circ}$ ), **carbon monoxide**  $\text{CO}$  (c.t.  $-40^{\circ}$ ), **methane**  $\text{CH}_4$  (c.t.  $-99^{\circ}$ ), and the six **inert gases** (p. 9), are the ones which

have low critical temperatures (*cf.* p. 166) and are **difficult to liquefy**.

Of the gases we have studied, the ones which are more or less easily liquefied are: hydrogen chloride (c.t.  $+52^{\circ}$ ), bromide, and iodide, chlorine (c.t.  $+141^{\circ}$ ), ozone, hydrogen sulphide (c.t.  $+100^{\circ}$ ), sulphur dioxide (c.t.  $+154^{\circ}$ ).

**The Solubilities of Gases.** — For the purpose of remembering the solubilities of gases in water, it is convenient to divide the gases into three classes. The following are the ones we have studied:

1. **Slightly soluble:** Oxygen (4 vol. : 100 at  $0^{\circ}$ ), hydrogen (2 : 100 at  $0^{\circ}$ ).

2. **Soluble:** Chlorine (2.6 vol. : 1 at  $10^{\circ}$ ), hydrogen sulphide (4.4 : 1 at  $0^{\circ}$ ).

3. **Very soluble:** Hydrogen chloride (505 vol. : 1 at  $0^{\circ}$ ), bromide (404 : 1) and iodide (1570 : 1), sulphur dioxide (69 : 1 at  $0^{\circ}$ ).

**Preparation of Sulphur Trioxide  $\text{SO}_3$ .** — Although the formation of sulphur trioxide  $\text{SO}_3$  is accompanied by the liberation of much heat, sulphur dioxide and oxygen, even when heated together, unite very slowly. Ozone, however, combines with the former readily.

The interaction of sulphur dioxide and oxygen is hastened by many substances, such as glass, porcelain, ferric oxide and, more especially, finely divided platinum, which remain themselves unchanged and simply act as catalytic agents. The contact process, as this is called, has been rendered available for the commercial manufacture of sulphur trioxide by Knietzsch (1901). The chief features of the process are: (1) The complete removal of arsenious oxide, dust, and other impurities derived from the calcining of pyrite or some other mineral sulphide, the minutest traces of which "poison" the catalytic agent and soon render it absolutely inoperative. (2) The preliminary passage of the cold mixture of gases over the outside of the pipes containing the contact agent. This removes part of the heat generated by the action,  $\text{SO}_2 + \text{O} \rightleftharpoons \text{SO}_3 + 22,600 \text{ cal.}$ , going on inside, and keeps the temperature of the interior at  $400^{\circ}$ . Below  $400^{\circ}$ , the union is too slow; above  $400^{\circ}$ , the reverse action is strengthened (van't Hoff's law, p. 305), and the union is incomplete. At  $400^{\circ}$ , 98–99 per cent of the materials unite; at  $700^{\circ}$ , only 60 per cent, at  $900^{\circ}$  practically none. Twice the quantity of oxygen theoretically needed is employed.

The vaporous product, mainly 1 vol.  $\text{O}_2$  to 2 vol.  $\text{SO}_3$  (gas), is

condensed by being led into 97-99 per cent sulphuric acid, and the concentration of the liquid is constantly maintained at this point by the regulated influx of water. Oleum (*q.v.*) is also made by omitting to add water. The trioxide is thus chiefly used for immediate conversion into sulphuric acid.

The process may be illustrated by placing some platinized asbestos\* in a tube (Fig. 88, p. 217), which is gently warmed, and introducing oxygen and sulphur dioxide through the limbs of the Y-tube. Dense fumes appear at the exit (see next par.).

It would seem to be simpler to dissolve the gaseous sulphur trioxide in water, to give sulphuric acid  $\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$ , rather than in 98 per cent sulphuric acid, but this cannot be done. The mixture  $\text{O}_2 + 2\text{SO}_3$  is very incompletely absorbed by water. When a bubble of this mixture enters water, the latter evaporates in the attempt to saturate the space occupied by the bubble with water vapor (p. 145 and Appendix IV). The water, however, combines with the sulphur trioxide to form a fog, consisting of droplets of liquid sulphuric acid, and so more and more water evaporates into the bubbles. The molecules of  $\text{SO}_3$ , so long as they remain gaseous, move with great velocity, namely 292 meters per second at room temperature, and still faster in this hot gaseous mixture. Hence, all the molecules that escape combination with the water vapor, strike the wall of the bubble, and combine with the water in a few seconds. The droplets of sulphuric acid, forming the fog, however, are not molecules but large aggregates of molecules. They do not therefore move like the molecules of a gas, but are absolutely stationary. Hence, after the gaseous sulphur trioxide has dissolved, the droplets of fog, carried by the excess of oxygen, can be bubbled through a whole series of vessels of water in succession without any appreciable number of the droplets being dissolved. The same fog can be shaken in a flask with water, violently and continuously, without any appreciable solution. When the water is thrown, by the shaking, through the oxygen, the oxygen is split up by the water, and driven about, but the fog particles move with the oxygen, so that the water never reaches them. On the other hand, when the mixture of gases bubbles through 98 per cent sulphuric acid, as is done in practice, there is no water available, the sulphur trioxide remains gaseous, and its rapidly moving molecules in a few seconds have all plunged into the sulphuric acid and combined with it, either uniting with the 1-3 per cent of

\* Asbestos, dipped in a solution of chloroplatinic acid and heated in the Bunsen flame:  $\text{H}_2\text{PtCl}_6 \rightarrow \text{Pt} + 2\text{HCl} \uparrow + 2\text{Cl}_2 \uparrow$ .

water present, or, when oleum is made, uniting with the sulphuric acid to form pyrosulphuric acid:  $\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}_2\text{O}_7$ .

This case affords an admirable illustration of the importance of physics in practical chemistry (p. 40). The chemical reaction occurs with water, but the physical condition of the fog of sulphuric acid prevents its dissolving and, if water were used in a factory, a large proportion of the sulphuric acid would pass with the excess of oxygen into the air and be lost. In fact, it would kill vegetation, and make life unbearable in the neighborhood. It is stated that the inventor of the contact process spent a year of time, and much money, in trying to find some way of using water to absorb the gas. Yet ten minutes' consideration of the physical situation would have shown that this was impossible, and the rest of the year could have been devoted to other work that offered some prospect of successful results.

Formerly sulphur trioxide was obtained by the distillation of impure ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{SO}_3$ . It may also be prepared by repeated distillation of concentrated sulphuric acid with a powerful drying agent, like phosphoric anhydride.

**Physical Properties.**— Sulphur trioxide  $\text{SO}_3$  is, at ordinary temperatures, fluid. The crystals, obtained by cooling, melt at  $14.8^\circ$ . The liquid boils at  $46^\circ$ , and is, therefore, exceedingly volatile at ordinary temperature. It fumes strongly when exposed to the air, in consequence of the union of the vapor with moisture and the production of minute drops of sulphuric acid.

A white crystalline variety of the substance, which in appearance closely resembles asbestos, is obtained when a trace of water has gained access to the oxide. The substance is dimorphous (p. 412). When heated to  $50^\circ$ , this passes into vapor of  $\text{SO}_3$  without melting. This white solid is the more stable and more familiar form of the trioxide.

**Chemical Properties.**— The vapor of sulphur trioxide, when heated, dissociates into sulphur dioxide and oxygen ( $400^\circ$ , 2 per cent;  $700^\circ$ , 40 per cent).

Sulphur trioxide is not itself an acid, but it is the anhydride of sulphuric acid. When placed in water it unites vigorously, causing a hissing noise due to the steam produced by the heat of the union. In consequence of its great tendency to combine with water, the liquid variety, which is the more active, removes the elements of this sub-

stance from materials which contain them in the proper proportions. Thus paper, which is largely cellulose  $(C_6H_{10}O_5)_n$ , and sugar  $C_{12}H_{22}O_{11}$ , are charred by it, and carbon is set free.

Just as sulphur trioxide unites with water to give hydrogen sulphate, so it combines vigorously with many oxides of metals, producing the corresponding sulphates:



The union of an oxide of a non-metal with the oxide of a metal, in this fashion, is a general method of obtaining salts (*cf.* p. 407).

**Oxygen Acids of Sulphur.** — Sulphurous and sulphuric acids have been mentioned frequently already. Next to them in importance come thiosulphuric acid and persulphuric acid. The compositions of the acids show their relationships:

Hyposulphurous acid,	$H_2S_2O_4$ .	Sodium hyposulphite,	$Na_2S_2O_4$ .
Sulphurous acid,	$H_2SO_3$ .	Sodium sulphite,	$Na_2SO_3$ .
Sulphuric acid,	$H_2SO_4$ .	Sodium sulphate,	$Na_2SO_4$ .
Thiosulphuric acid,	$H_2S_2O_3$ .	Sodium thiosulphate,	$Na_2S_2O_3$ .
Persulphuric acid,	$H_2S_2O_8$ .	Sodium persulphate,	$Na_2S_2O_8$ .

Thiosulphuric acid (Gk. *θειον*, sulphur) is so named because it contains one unit of sulphur in place of one of the units of oxygen of sulphuric acid. Note that when the names of the acids end in *ous* and *ic*, the names of the salts end in *ite* and *ate*, respectively. Besides the above we have also the polythionic acids, namely: Dithionic acid  $H_2S_2O_6$ , trithionic acid  $H_2S_3O_6$ , tetrathionic acid  $H_2S_4O_6$ , and pentathionic acid  $H_2S_5O_6$ .

On account of its commercial importance and the interest attaching to its method of manufacture and to its properties, we may first discuss sulphuric acid. We shall then be able to dispose of the remaining acids in a much briefer fashion.

### SULPHURIC ACID $H_2SO_4$

Although salts of sulphuric acid, such as calcium sulphate, are exceedingly plentiful in nature, the preparation of the acid by chemical action upon the salts is not practicable. The sulphates, indeed, interact with all acids, but the actions are reversible. The completion of the action by the plan used in making hydrogen chloride (p. 206), involving the removal of the sulphuric acid by distillation,

would be difficult on account of the involatility of this acid. It boils at  $330^{\circ}$ ; and suitable active acids, less volatile still, which might be used to liberate it, do not exist. We are therefore compelled to build up sulphuric acid from its elements.

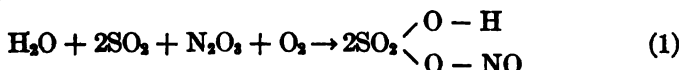
The union of sulphur dioxide and oxygen by the **contact process**, and combination of the trioxide with water (p. 428), is the best method for making a highly concentrated acid. For obtaining ordinary "oil of vitriol," however, the **chamber process** is still used extensively.

**History of Sulphuric Acid Manufacture.** — Impure forms of sulphuric acid have been known for many centuries. In the fifteenth century it was made by distilling ferrous sulphate with sand. The product, however, contained much water and sulphur dioxide. The first successful preparation of the substance commercially was made by Ward at Richmond-on-the-Thames (1758). The process consisted in burning a mixture of sulphur and saltpeter  $\text{KNO}_3$  in a ladle suspended in a large glass globe partially filled with water. The gases which were evolved contained large quantities of sulphur dioxide and oxides of nitrogen, which, by interaction with atmospheric oxygen and water (see below), produced the sulphuric acid. The solution which was obtained, although it could be prepared of any desired concentration by the burning of a sufficient number of charges, was far from pure and was expensive, bringing thirteen shillings (\$3.25) per pound. Subsequently a chamber lined with lead was substituted for the glass vessel. This reduced the price to about two shillings and sixpence (\$0.60) per pound. The same principles are used in the modern "chamber process."

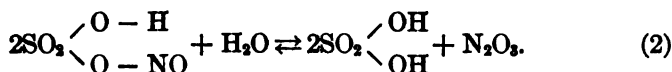
**Chemistry of the Chamber Process.** — The gases, the interactions of which result in the formation of sulphuric acid, are: water vapor, sulphur dioxide, nitrous anhydride  $\text{N}_2\text{O}_3^*$  (*q.v.*), and oxygen. These are obtained, the first by injection of steam, the second usually by the burning of pyrite, pyrrhotite ( $\text{FeS}$ ), or some other mineral sulphide, the third from nitric acid  $\text{HNO}_3$ , and the fourth by the introduction of air. The gases are thoroughly mixed in large leaden chambers, and the sulphuric acid condenses and collects upon the floors. In spite of elaborate investigations, instigated by the exten-

\* This gas is unstable, breaking up in part into nitric oxide  $\text{NO}$  and nitrogen tetroxide  $\text{NO}_2$ :  $\text{N}_2\text{O}_3 \rightleftharpoons \text{NO} + \text{NO}_2$ . In the process here discussed, however, the mixture behaves as if it were all  $\text{N}_2\text{O}_3$ , and so only nitrous anhydride is named in this connection.

sive scale upon which the manufacture is carried on and the immense financial interests involved, some uncertainty still exists in regard to the precise nature of the chemical changes which take place. According to Lunge, supporting the view first suggested by Berzelius, the greater part of the product is formed by two successive actions, the first of which yields a complex compound that is decomposed by excess of water in the second:



The group  $-\text{NO}$  is found in many compounds. Here, if it were displaced by hydrogen, sulphuric acid would result. Hence this compound is called **nitrosylsulphuric acid**.



The equations (1) and (2) are not partial equations for one interaction, but represent distinct actions which can be carried out separately. In a properly operating plant, indeed, the nitrosylsulphuric acid is not observed. But when the supply of water is deficient, white "chamber crystals," consisting of this substance, collect on the walls.

The explanation of the success of this seemingly roundabout method of getting sulphuric acid is as follows: The direct union of sulphur dioxide and water to form sulphurous acid is rapid, but the action of free oxygen upon the latter,  $2\text{H}_2\text{SO}_3 + \text{O}_2 \rightarrow 2\text{H}_2\text{SO}_4$ , is exceedingly slow. Reaching sulphuric acid by the use of these two changes, although they constitute a direct route to the result, is not feasible in practice. On the other hand, both of the above actions, (1) and (2), happen to be much more speedy, and so, by their use, more rapid production of the desired substance is secured at the expense of a slight complexity. It may be added that the heat finally given out in the formation of one formula-weight of sulphuric acid is exactly the same in amount whether nitrous anhydride intervenes or not (*cf.* p. 100).

The progress of the first action is marked by the disappearance of the brown nitrous anhydride and, on the introduction of water, the completion of the second results in the reproduction of the same substance. It would thus seem as if the nitrous anhydride should take part an indefinite number of times in these changes and so facilitate the conversion of an unlimited amount of sulphur dioxide, oxygen,



and water into sulphuric acid, without diminution of its quantity. In practice, however, certain subsidiary actions take place, such as, for example, the reduction of some nitrous anhydride to nitrous oxide  $N_2O$ , which permanently remove a part of the material from participation in the cycle.

The loss of nitrous anhydride is made good by the introduction of nitric acid vapor into the chamber. This acid is secured by the action of concentrated sulphuric acid upon commercial sodium nitrate  $NaNO_3$ :



On account of the volatility of the nitric acid, a moderate heat is sufficient to remove it from admixture with the other substances, and its vapor is swept along with the other gases into the apparatus. The initial action which the nitric acid undergoes:



may be written to show the anhydride of nitric acid:



The two molecules of water, one actually, the other potentially, present, with the two molecules of sulphur dioxide, can furnish two molecules of sulphurous acid  $H_2SO_3$ . The  $N_2O_5$  in passing to the condition  $N_2O_3$  gives up the two units of oxygen required to convert this sulphurous acid into sulphuric acid.

**Details of the Chamber Process.**—The sulphur dioxide is produced in a row of small furnaces *A* (Fig. 112), the structure of which depends upon the nature of the substance employed to yield this fundamental constituent of sulphuric acid. When good pyrite is used, the ore burns unassisted (p. 424), while impure pyrite and zinc-blende  $ZnS$  have to be heated, to a greater or less degree, artificially, to maintain the combustion. The gases from the various furnaces pass into one long dust flue, in which they are mingled with the proper proportion of air, and have an opportunity to deposit oxides of iron and of arsenic and other materials which they transport mechanically. From this flue they enter the Glover tower *G*, in which they acquire the oxides of nitrogen. Having secured all the necessary constituents, excepting water, and having been reduced very considerably in temperature, the gases next enter the first of the lead chambers, large structures, from three to five in number, lined com-

pletely with sheet lead. They vary in size, measuring as much as  $100 \times 40 \times 40$  feet, and sometimes having a total capacity of 150,000 to 200,000 cubic feet. As the gases drift through these chambers they are thoroughly mixed, and an amount of water considerably in excess of that required by the chemical reactions, is injected in the form of steam at various points. The temperature in the first chamber is

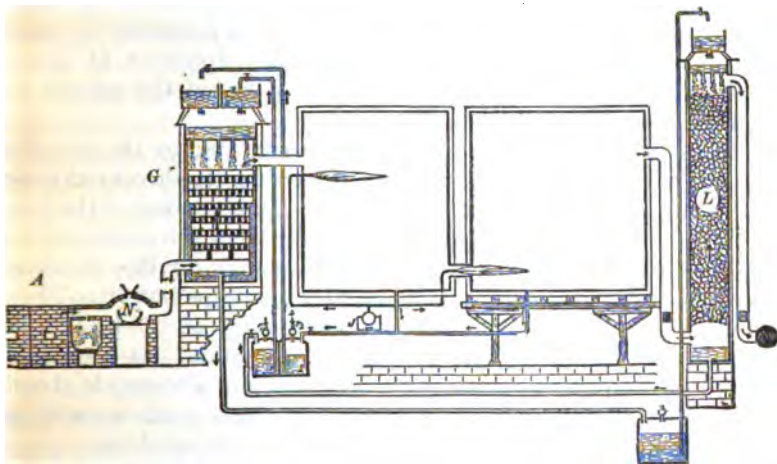


FIG. 112.

maintained at  $50^{\circ}$  to  $65^{\circ}$ , while in the last chamber it is about  $15^{\circ}$  above that of the outside air. The acid, along with the excess of water, condenses and collects upon the floor of the chamber, while the unused gases, consisting chiefly of nitrous anhydride and a very large amount of nitrogen, derived from the air originally admitted, find an exit into the Gay-Lussac tower *L*.

This is a tower about fifty feet in height, filled with tiles, over which concentrated sulphuric acid continually trickles from a reservoir at the top. The object of this tower is to catch the nitrous anhydride and enable it to be reemployed in the process. This is accomplished by a reversal of action (2) above. The acid which accumulates in the vessel at the bottom of this tower contains the nitrosylsulphuric acid, and by means of compressed air is forced through a pipe up to a vessel at the top of the Glover tower *G*. When this "nitrous vitriol" is mixed with dilute sulphuric acid from a neighboring vessel, by allowing both to flow down into the tower, the nitrous anhydride is once more set free by the interaction of the water in the dilute acid

(action (2)). The Glover tower is filled with broken quartz or tiles, and the heated gases from the furnace acquire in it their supply of nitrous anhydride. Their high temperature causes a considerable concentration of the diluted sulphuric acid as it trickles downward. The acid, after traversing this tower, is sufficiently strong to be used once more for the absorption of nitrous anhydride.

To replace the nitrous anhydride inevitably lost by reduction to nitrous oxide and otherwise, fresh nitric acid is furnished by small open vessels *N*, containing sodium nitrate and sulphuric acid, placed in the flues of the pyrite-burners. About 4 kg. of the nitrate are consumed for every 100 kg. of sulphur.

The immense size of the chambers is necessitated by the fact that the chemical action, although much quicker than the direct oxidation of sulphurous acid, is after all rather slow. The presence of the large amount of atmospheric nitrogen, which diminishes the concentration of all the interacting substances, partly accounts for this slowness. The acid which accumulates upon the floors contains but 60 to 70 per cent of sulphuric acid, and has a specific gravity of 1.5–1.62. The excess of water is used to facilitate the second action. It is required also in order that the acid upon the floor may not afterwards absorb and retain the nitrous anhydride, for this substance combines with an acid containing more than 70 per cent of hydrogen sulphate.

This crude sulphuric acid is applicable directly in some chemical manufactures, such as the preparation of superphosphates (*q.v.*) used in large amounts as a fertilizer. In most cases, however, a more concentrated sulphuric acid is required. The concentration is effected in the first place by evaporation in pans lined with lead, which are frequently placed over the pyrite-burners in order to economize fuel. The evaporation in lead is carried on until a specific gravity 1.7, corresponding to 77 per cent concentration, is reached. Up to this point the sulphate of lead formed by the action of the sulphuric acid produces a crust which protects the metal from further action. The insoluble sulphate of lead, however, becomes more soluble in sulphuric acid the more concentrated the acid is, and the higher, therefore, its boiling-point. When a stronger acid is required, the water is usually driven out by heating the sulphuric acid in vessels of porcelain or platinum, or even of cast iron. Iron acts upon *dilute* sulphuric acid, displacing the hydrogen-ion, but not upon the concentrated acid, which is not ionized. Commercial sulphuric acid, *oil of vitriol*, has a specific gravity 1.83–1.84, and contains about 93.5 per cent of sulphuric acid.

**Physical Properties.** — Pure hydrogen sulphate (100 per cent) has a sp. gr. 1.85 at 15°. When cooled, it crystallizes (m.-p. 10.5°). At 150°–180° the acid begins to fume, giving off sulphur trioxide. At 330° it boils, but loses more sulphur trioxide than water, and finally leaves in the retort an acid of constant (p. 211) boiling-point (338°) and constant composition (98.33 per cent).

When hydrogen sulphate is mixed with water, a considerable evolution of heat takes place. This heat of solution (p. 203) receives progressively diminishing increments as more water is added, until a very great dilution has been reached. The total is 39,170 cal. This heat of solution has not been accounted for quantitatively, but a part of it is due to the heat given out in connection with the ionization of the hydrogen sulphate. The pure substance, and the concentrated acid, absorb water greedily from the moisture in the air (or other gas), and so are used for drying gases.

**Impurities.** — Commercial sulphuric acid is frequently brown in color on account of the presence of fragments of straw which have become charred and finally completely disintegrated. It contains also lead sulphate, which appears as a precipitate when the acid is diluted, as well as arsenic trioxide and oxides of nitrogen in combination, and many other foreign substances in small quantities. The pure sulphuric acid employed in chemical laboratories has received special treatment for the removal of these ingredients.

**Chemical Properties of Hydrogen Sulphate  $H_2SO_4$ .** — 1. The compound is **not** exceedingly **stable**, for dissociation into water and sulphur trioxide begins far below the boiling-point (cf. p. 437). The vapor of the acid boiling at 338° contains only 66 per cent of  $H_2SO_4$  and 34 per cent of  $H_2O + SO_3$ , which recombine when the vapor is cooled. The dissociation is practically complete at 416°, as is shown by the density of the vapor. When raised suddenly to a red heat it is broken up completely into water, sulphur dioxide, and oxygen.

2. When sulphur trioxide is dissolved in hydrogen sulphate, **pyro-sulphuric acid**  $H_2S_2O_7$ , a solid compound, is obtained. Hydrogen sulphate containing 20 per cent of pyro-sulphuric acid is known as "oleum," and is employed in chemical industries. The old "fuming," or "Nordhausen," sulphuric acid contained 10–20 per cent of extra sulphur trioxide. The salts of disulphuric acid may be made by strongly heating the acid sulphates, for example:

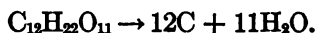


In view of this mode of preparation by the aid of heat, they were named **pyrosulphates** (Gk.  $\pi\rho$ , fire). When they are dissolved in water, the acid sulphates are reproduced by reversal of the foregoing reaction.

3. With salts which it does not oxidize, hydrogen sulphate **reacts by double decomposition** and sets free the corresponding acid. The actions are always reversible ones; but where the new acid is volatile, as in the case of hydrogen chloride (p. 206), we are furnished with one of the cheapest means of preparing acids.

Since hydrogen sulphate is **dibasic** (p. 372), it forms both **acid** and neutral salts, such as  $\text{NaHSO}_4$  and  $\text{Na}_2\text{SO}_4$ . The acid sulphates are called also bisulphates, because they contain twice as large a proportion of  $\text{SO}_4$  to metallic element, and require twice as much sulphuric acid for their preparation as do the neutral sulphates.

4. Sulphuric acid combines vigorously with water to form at least one rather stable **hydrate**,  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (m.-p.  $8^\circ$ ). On this account, sulphuric acid is able to take the elements of water from compounds containing hydrogen and oxygen, especially those containing these elements in the proportion  $2\text{H} : \text{O}$ . Thus paper, which is largely cellulose  $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ , wood which contains much cellulose, and sugar  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  are charred by it, and carbon is set free:



The same tendency is enlisted to promote chemical actions in which water is formed, particularly in connection with the manufacture of nitroglycerine (*q.v.*) and guncotton (*q.v.*). For the same reason, sulphuric acid is used in drying gases with which it does not interact.

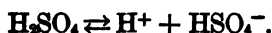
5. On account of the large quantity of oxygen which hydrogen sulphate contains, and its instability when heated, it behaves as an **oxidising agent**. This property has already been illustrated in connection with the action of the acid upon carbon, sulphur, and copper (p. 425), hydrogen sulphide (p. 416), zinc (p. 119), and, particularly, hydrogen iodide (p. 277) and hydrogen bromide (p. 272). The sulphuric acid is itself reduced to sulphur dioxide, and even to free sulphur or hydrogen sulphide. The metals, from the most active down to silver (p. 404), are capable of reducing it, the sulphates\* being formed. The more active metals, like zinc, reduce it to hydrogen

\* Note that the sulphates, and *not* the oxides of the metals, are produced. Oxides of metals could not be formed in concentrated sulphuric acid, because they interact with the latter much more vigorously than do the metals, to give the sulphates (*cf.* p. 213).

sulphide (p. 416), the less active, like copper, give sulphur dioxide (p. 425). Hydrogen is not liberated, because no hydrogen-ion is present in concentrated sulphuric acid. Gold and platinum alone are not attacked, and hence their use in making sulphuric acid stills. Free hydrogen itself is oxidized to water when passed into hydrogen sulphate at 160°:  $\text{SO}_2(\text{OH})_2 + \text{H}_2 \rightarrow \text{SO}_2 + 2\text{H}_2\text{O}$ .

Concentrated sulphuric acid is **used** in almost all chemical industries: for example, to give sodium sulphate, as a stage in the Le Blanc process for the manufacture of soda; in the refining of petroleum; in the manufacture of fertilizers, such as superphosphate; in the preparation of nitroglycerine and guncotton, where it assists the action by removing water; and in the production of coal-tar dyes.

**Ionization of Dibasic Acids.**—An acid containing but one unit of hydrogen in its molecule can give but two kinds of ions. Thus, chloric acid gives only  $\text{H}^+$  and  $\text{ClO}_3^-$ . When more than one hydrogen unit is present, however, more than two kinds of ions are formed. Thus, sulphuric acid,  $\text{H}_2\text{SO}_4$ , produces, in the first place, hydrosulphate-ion:



The latter is also an acid, but is **considerably less active** than sulphuric acid. Hence, the further dissociation of this ion:  $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{=}$ , lags considerably behind the primary dissociation. In concentrated solutions of the acid there is, therefore, much  $\text{HSO}_4^-$  present. In very dilute solutions, however,  $\text{SO}_4^{=}$  predominates. We know that  $\text{HSO}_4^-$  is a weaker acid, and is dissociated with greater difficulty by water, because acid salts, like  $\text{KHSO}_4$ , which give this ion, are much weaker acids than are acids like  $\text{HCl}$  and  $\text{HClO}_3$ , with which the substance  $\text{HSO}_4^-$  might fairly be compared. This behavior is not peculiar to sulphuric acid, but is shown by all acids containing more than one hydrogen unit in the molecule (*cf.* Hydrogen sulphide, p. 417).

**Chemical Properties of Aqueous Hydrogen Sulphate.**—The solution of sulphuric acid is a mixture whose components are: undissociated molecules  $\text{H}_2\text{SO}_4$ , hydrogen-ion  $\text{H}^+$ , hydrosulphate-ion  $\text{HSO}_4^-$ , and sulphate-ion  $\text{SO}_4^{=}$ . The chemical properties shown by the solution are those of one or other of these components, according to circumstances.

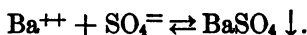
Except in concentrated solutions (normal or stronger) the oxidizing effects of the undissociated, molecular substance are not encountered. The temperature of the diluted acid, even when boiling, is not high enough for the purpose. In fairly strong solutions, hydrosulphate-ion is plentiful and shows itself in the results of electrolysis (see p. 449).

The presence of hydrogen-ion is shown by all its usual properties (p. 373). In the following table the proportion of the whole of the hydrogen existing in the form of hydrogen-ion (column five) and its concentration (column six), taking a normal solution of hydrogen-ion containing 1 g. per liter as standard, are shown (*cf.* pp. 182 and 366). The first three columns give the concentration of the sulphuric acid as a whole, in terms (first column) of the volume (liters) of liquid containing one equivalent ( $\frac{1}{2}\text{H}_2\text{SO}_4 = 49$  g.), in terms (second column) of a normal solution as standard, and by per cent (third column), respectively. The fourth column shows the conductivity (p. 365).

	$\text{H}_2\text{SO}_4$	PER CENT $\text{H}_2\text{SO}_4$	$\lambda_v$	$\lambda_v/\lambda_\infty$	$\text{H}^+$
0.1	10N	38.00	70	0.18	1.8N
1	N	4.79	198	0.51	0.51N
10	0.1N	0.48	225	0.58	0.058N
100	0.01N	0.05	308	0.79	0.0079N
1000	0.001N	0.005	361	0.93	0.00093N
$\infty$	0	0.00	388	1.00	0.00

Column 5 thus states that in a normal solution 51 per cent, and in a centi-normal solution 79 per cent of the hydrogen is ionic.

Sulphate-ion  $\text{SO}_4^{=}$ , which is found also in solutions of all neutral and acid sulphates, unites with all positive ions. The product, when insoluble, appears as a precipitate. The introduction of barium ions, for example, by adding a solution of barium nitrate or chloride, is employed as a test for sulphate-ion:

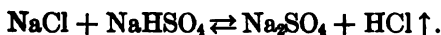


Since there are other barium salts which are insoluble in water (see Table of solubilities), but no common ones which are not decomposed by acids, dilute nitric acid is first added to the solution supposed to contain the sulphate-ion. The other ions, if present, then give no precipitate with barium-ion.

Dilute sulphuric acid is used for many purposes. Thus it forms the liquid in the lead storage battery, and is employed for cleaning sheet iron before tinning and galvanizing.

**Sulphates.**—The **acid sulphates**, known also as **bisulphates** (p. 438), may be produced either by adding to dilute sulphuric acid half an equivalent of a base, and evaporating:  $\text{NaOH} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{O} + \text{NaHSO}_4$ , or by actions in which another acid is displaced by concentrated sulphuric acid, as in making hydrogen chloride (p. 206). These salts are acid in reaction, as well as in name (*cf.* p. 401), because  $\text{HSO}_4^-$ , although a weak, is not a feeble acid. When heated, they yield pyrosulphates (p. 438).

The **normal** (or **neutral**) **sulphates** are obtained by complete neutralization and evaporation, or by the second of the above methods when a sufficient amount of the salt and a higher temperature are used:



They are often made also by precipitation, by oxidation of a sulphide at a high temperature,  $\text{PbS} + 2\text{O}_2 \rightarrow \text{PbSO}_4$ , or by addition of sulphur trioxide to the oxide of a metal (p. 431).

Normal sulphates of many heavy metals decompose at a red heat, those of the trivalent metals giving off sulphur trioxide (p. 430), and those of some bivalent metals (*e.g.*, Mn, Ni, Co), giving sulphur dioxide and oxygen. The sulphates of potassium, sodium, and others of the more active metals, and lead sulphate, however, are not affected by heating.

When a sulphate, or indeed any salt of a sulphur acid, is heated strongly with carbon, the oxygen is removed and a sulphide remains:  $\text{Na}_2\text{SO}_4 + 4\text{C} \rightarrow \text{Na}_2\text{S} + 4\text{CO}$ . Upon this is founded a general **test** for the presence of sulphur in any substance. The material to be tested is mixed with sodium carbonate. A small amount of the mixture is placed on the end of a match, which has been charred and rendered partially incombustible by previous application of sodium carbonate. When the end of the match is now held in the reducing part of the Bunsen flame, the compound of sulphur, if it contains oxygen, is reduced to the form of sulphide. This, by interaction with the carbonate, gives sodium sulphide,  $\text{Na}_2\text{S}$ . When the product of the reduction is placed upon a silver coin and moistened, the sodium sulphide, if present, produces a black stain of silver sulphide. This is known as the **hepar test**, *hepar* being an old name for a sulphide.

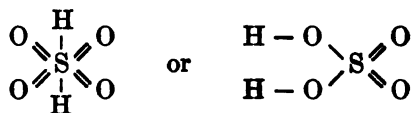
**Constitution of Hydrogen Sulphate.**—The formula which we assign to sulphur trioxide is  $\text{O} = \text{S} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{O} \end{smallmatrix}$ . It is in general our



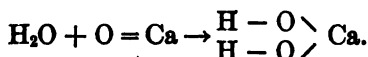
desire to use the smallest possible valence, but here no reduction can be effected below the value 6 for the sulphur, unless we join the oxygen units to one another, as in the formula  $O = S \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$ . This,

however, would suggest a relationship to hydrogen peroxide,  $\begin{smallmatrix} O - H \\ | \\ O - H \end{smallmatrix}$

which is not confirmed, for hydrogen peroxide cannot be made from sulphuric acid. Assuming, therefore, the above formula for sulphur trioxide, the addition of the elements of water to it in the simplest fashion results in the structures:

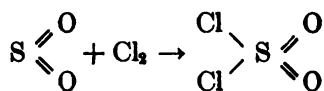


The second of these two modes of disposing of the water is the one which, in parallel cases, is usually most feasible. Hardly any alternative to it is possible, for example, in representing the action in which quicklime is slaked (p. 149):



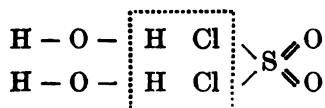
This represents the change with little derangement of the original structure and without alteration in the valence, while the first unwarrantably increases the valence to ten. There are other objections to the first formula. In it the hydrogen is supposed to unite more immediately with the sulphur, whereas, when the free elements are concerned, hydrogen actually combines more readily with oxygen, and forms a more stable compound with it than with sulphur. Again, compounds like hydrogen sulphide,  $H - S - H$ , in which the hydrogen is undoubtedly united to sulphur, are but slightly ionized, and are feeble acids, while hydrogen sulphate is highly ionized.

Another fact is more satisfactorily accounted for by the second formula. The addition of chlorine to sulphur dioxide must be shown thus:



for chlorine has a much greater tendency to unite with sulphur than with oxygen. When the product, sulphuryl chloride, is brought in

contact with water, sulphuric acid and hydrogen chloride are produced. Since water has the formula  $\text{H} - \text{O} - \text{H}$ , and two molecules of water are used, this action is most simply accounted for, with the minimum of disturbance in both molecules, by imagining the operation to take place as follows:

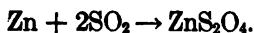


The hydrogen chloride is eliminated, and the other units of hydrogen, originally without doubt attached to oxygen in the water, may be presumed to be still connected with that oxygen when they enter the molecule of hydrogen sulphate.

This illustration shows the sort of reasoning, based upon the chemical properties and the modes of formation of a substance, which lead us to the devising of an appropriate graphic or structural formula (*cf.* p. 322). The latter is not supposed to represent the actual physical structure of the molecule, but simply to be a diagrammatic representation of the chemical relations of the constituents and of the chemical behavior of the whole. Formulæ of this kind are in continual use in the study of the compounds of carbon, but are seldom required outside of that region.

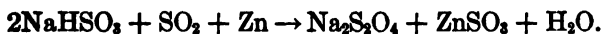
#### OTHER ACIDS OF SULPHUR

**Hyposulphurous Acid  $\text{H}_2\text{S}_2\text{O}_4$ .**—The zinc salt of this acid crystallizes out when zinc dust acts upon a solution of sulphur dioxide in absolute alcohol:



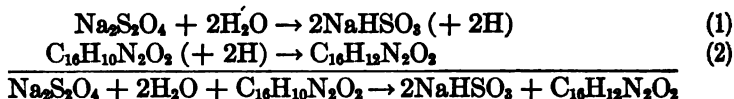
Moissan found that when sulphur dioxide was led over sodium hydride, sodium hyposulphite was formed:  $2\text{NaH} + 2\text{SO}_2 \rightarrow \text{Na}_2\text{S}_2\text{O}_4 + \text{H}_2$ .

Commercially, a solution containing the sodium salt is made by the interaction of zinc with a solution of sodium bisulphite charged with excess of sulphur dioxide:



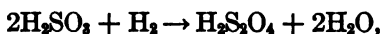
The salts are rapidly oxidized by the air, giving sulphites and then sulphates. The above solution of sodium hyposulphite is used in indigo dyeing, and with other vat dyes, on account of its high reducing

power. Indigo  $C_{16}H_{10}N_2O_2$ , which is insoluble, is reduced by the salt to indigo-white  $C_{16}H_{12}N_2O_2$  which passes into solution:



When cloth saturated with the mixture, however, is exposed to the air, the indigo-white undergoes oxidation, and blue, insoluble indigo is formed once more (see Dyeing).

The acid is formed when sulphurous acid surrounds the negative electrode in an electrolytic cell:



and was first named (after the discoverer) Schützenberger's acid. The sodium salt is formed in the same way from sodium bisulphite.

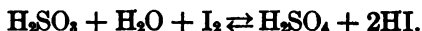
**Sulphurous Acid.**—This term is applied to the solution of sulphur dioxide in water. A portion of the sulphur dioxide remains dissolved physically, while another portion is in combination with the water, forming sulphurous acid. This in turn is ionized, and chiefly, after the manner of the weaker dibasic acids, into two ions,  $H^+$  and  $HSO_3^-$ . A little  $SO_3^{=}$  is formed from the latter. There are thus in such a solution four mutually dependent equilibria:



When the solution is heated, uncombined sulphur dioxide is disengaged as a gas. The equilibria being thus disturbed, the ions of the acid unite, the acid molecules decompose, and soon all the above actions are completely reversed and the whole of the gas passes off. Conversely, when a base furnishing hydroxide ions is added to the solution of the acid, the hydrogen ions disappear, forming water, and the above actions all proceed in a forward direction until, with a half-equivalent of the base, the whole of the material has been converted into the form  $HSO_3^-$ , in association, of course, with the positive ions of the base. With a full equivalent, neutralization follows and  $SO_3^{=}$  is the product.

**Properties of Sulphurous Acid.**—The acid is so unstable that it cannot be obtained excepting in solution in water. Chemically it is a comparatively weak acid.

As a **reducing agent**, it is slowly oxidized by free oxygen, turning into sulphuric acid. Sugar and glycerine act as **negative contact agents** and make the oxidation much *slower*. It is rapidly oxidized by active oxidizing agents. Thus, when free halogens are added to the solution, sulphuric acid and the hydrogen halide are formed:



In the particular case of iodine this action takes place only in very dilute solution, since concentrated sulphuric acid decomposes hydrogen iodide (*cf.* p. 277) and the action is reversed. This interaction is used in chemical analysis as a means of estimating the quantity of sulphurous acid in a liquid (*cf.* p. 277).

Hydrogen peroxide, potassium permanganate, and other oxidizing agents convert the substance into sulphuric acid likewise. It should be noted that in these oxidations we have, not an addition of oxygen to  $\text{SO}_2$ , but to the  $\text{SO}_3^=$  or  $\text{HSO}_3^-$  ion of the acid, whereby it passes into the  $\text{SO}_4^=$  ion of sulphuric acid. The ion is much more easily oxidized than is free sulphur dioxide itself.

When heated alone, in a sealed glass tube ( $150^\circ$ ), the acid reduces part of itself to sulphur, and a part is oxidized to sulphuric acid:



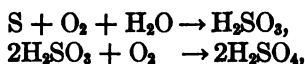
Sulphurous acid has the power of **uniting directly** with many organic coloring matters and, since the products of this union are usually colorless, it is employed as a bleaching agent. It is especially useful with materials like silk, wool, and straw, which are likely to be destroyed by hypochlorous acid. Sunlight causes the dissociation of these colorless compounds, and so, with use, straw hats slowly recover their original color. As a disinfectant it acts by addition likewise.

As a **dibasic acid**, sulphurous acid forms normal salts like  $\text{Na}_2\text{SO}_3$ , and acid salts like  $\text{NaHSO}_3$ .

**Consecutive Reactions.** — There are many chemical reactions that proceed in two stages, which can be carried out separately. This is the case with the two reactions used in the chamber process (p. 433). The actions are **consecutive** (p. 272), because the second uses materials produced by the first. It may be noted that, if the second action is as speedy as the first, or speedier, then no intermediate products will be detectable. This is the case with the chamber process reactions, when sufficient steam is introduced, for under these circumstances no solid nitrosylsulphuric acid is

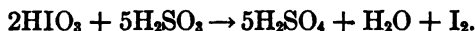
deposited. If the second reaction is slower than the first, then the products of the first reaction will accumulate, and become noticeable.

The conception of consecutive reactions enables us to understand and remember some facts. For example, it was mentioned that when dry sulphur is oxidized, we obtain sulphur dioxide, but when moist sulphur is oxidized, by the air or otherwise, the only product is sulphuric acid (p. 414). This change may be conceived of as proceeding in two stages:



which would be consecutive reactions. Since oxidation of solid sulphur can proceed only on the surface, it is slow. Since the sulphurous acid is dissolved, and every molecule of it is accessible to the dissolved oxygen, or oxidizing agent, the second action should be speedier and consume the product of the first action as fast as it is formed. It is, therefore, quite natural that no sulphurous acid should be detectable when water (or its vapor) is present.

**Illustration of the Effect of Concentration on Speed of Interaction.**—The oxidation of sulphurous acid by iodic acid  $\text{HIO}_3$  may be used to show [Lect. exp.] the effect of concentration on the speed of an action (p. 291). The iodic acid may most readily be made by dissolving potassium iodate  $\text{KIO}_3$  and sulphuric acid together in water, in such quantities as would give a  $N/2$  solution of each. When 1 c.c. of this  $N/2$  iodic acid is added to 100 c.c. of filtered starch emulsion, and the whole is mixed with an equal volume of water containing 1 c.c. of  $N/2$  sulphurous acid, the blue color produced by the liberated iodine appears suddenly after the lapse of a minute or more:



With double the above quantities in the same amount of water, that is, with double concentrations, the speed of the action is greatly increased and the iodine becomes visible in less than half the time.

**Sulphites.**—The acid sulphites of the alkali metals (i.e., of potassium and sodium) are acid in reaction, owing to the appreciable dissociation of the ion  $\text{HSO}_3^-$ . The acid being a weak one, however, solutions of the normal salts,  $\text{Na}_2\text{SO}_3$ , etc., are alkaline towards litmus

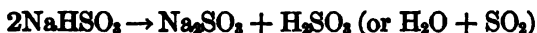
(p. 399). The sulphites are readily decomposed by acids giving free sulphurous acid, and the latter decomposes, yielding sulphur dioxide (p. 424).

Calcium bisulphite solution,  $\text{Ca}(\text{HSO}_3)_2$ , is used to dissolve the lignin out of wood chips employed in the manufacture of paper. About 30 per cent of the wood is lignin. The rest is cellulose  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , and constitutes the prepared pulp.

When heated, sulphites undergo decomposition. The sulphates, being the most stable of *all* the salts of sulphur acids, are formed when the salts of *any* of those acids are decomposed by heating. The nature of the particular salt determines what other products shall appear. Here, one molecule of the sulphite furnishes three atoms of oxygen, sufficient to oxidize three other molecules, and leaves one molecule of sodium sulphide behind (compare effect of heating sulphurous acid, *ibid.*, p. 445):



The acid sulphites (bisulphites) first lose sulphurous acid, before changing in this way. Thus, sodium-hydrogen sulphite begins by decomposing as follows:



and at a higher temperature the sulphite  $\text{Na}_2\text{SO}_3$  decomposes as explained above.

The acid salts of volatile acids, when heated, all decompose in this way (*cf.* pp. 281, 447).

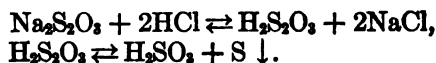
The sulphites are as readily **oxidized** as is the acid itself. They are slowly converted, both in solution and in the solid form, by the influence of the oxygen of the air, into sulphates. It is interesting to note that the addition of sugar or glycerine to a solution of a sulphite reduces the speed of oxidation by free oxygen very markedly. These substances act as contact agents; and the present case shows that agents of this kind may not only increase the speed of actions, which is their usual function, but may also have a restraining influence.

**Thiosulphuric Acid  $\text{H}_2\text{S}_2\text{O}_3$ .**—This acid is not known in the free condition, but its salts are in common use in the laboratory and commercially. Sodium thiosulphate, for example, is prepared by boiling a solution of sodium sulphite with free sulphur. The action is something like the addition of oxygen to sulphurous acid:



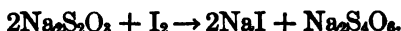
The product, thiosulphate of sodium, is used in photography as a solvent for salts of silver (fixing bath), and is commonly (but incorrectly) called "hypo."

By the addition of acids to a solution of sodium thiosulphate, the thiosulphuric acid is set free, but the latter instantly decomposes, giving a precipitate of sulphur:

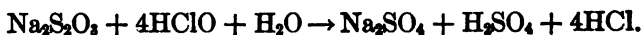


Even carbon dioxide from the air, giving carbonic acid (*q.v.*), produces this effect slowly in fixing solutions. The actions being reversible, preliminary addition of a sulphite to the solution helps to sustain the reverse action, in which sulphurous acid is a factor, and so preserves the solution. The delay in the appearance of the precipitate of sulphur in dilute solutions is due to the temporary existence of a supersaturated solution (*cf.* p. 193) of the free element. This is shown by the fact that instant neutralization of the free acid does not prevent the ultimate appearance of the sulphur.

Iodine acts upon sodium thiosulphate solution, giving sodium tetrathionate:



This action is used, by employment of a standard solution of sodium thiosulphate, for estimating quantities of free iodine in analysis. The disappearance of the color of the latter indicates that a sufficient amount of the salt has been employed. When chlorine-water (p. 223) is used, the oxidation is more complete. The products are sodium sulphate, sulphuric acid, and hydrochloric acid:



In consequence of the very great amount of free chlorine which the sodium thiosulphate is thus able to transform, it is employed, as *antichlor*, for the purpose of removing chlorine from bleached fabrics.

**Persulphuric Acid  $\text{H}_2\text{S}_2\text{O}_8$ .** — The salts of this acid are coming into use for commercial purposes and for "reducing" negatives in photography. When a discharge of electricity is passed through a mixture of sulphur trioxide and oxygen, drops of liquid are formed which appear to have the composition  $\text{S}_2\text{O}_7$ , and when dissolved in water give dilute persulphuric acid,  $\text{S}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S}_2\text{O}_8$ . More significant of its relations is its formation, to some extent, when

concentrated sulphuric acid and a strong solution of hydrogen peroxide are mixed:



This action is reversible.\* Under some circumstances, particularly by using pure (100 per cent) hydrogen peroxide and sulphur trioxide, a monobasic acid, monopersulphuric acid (Caro's acid, m.-p.  $45^\circ$ ) is formed:  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightleftharpoons \text{H}_2\text{SO}_5 + \text{H}_2\text{O}$ . Interesting in its way, also, is its production in the electrolysis of aqueous sulphuric acid:

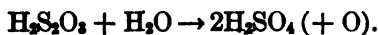


This action is most conspicuous in rather concentrated (50 per cent) solutions, in which hydrosulphate-ion is plentiful (cf. p. 439), and when a small anode, resulting in severe crowding of the  $\text{HSO}_4$  radicals as they are liberated, is employed. The salts were first prepared by electrolyzing ammonium or sodium-hydrogen sulphate  $\text{NaHSO}_4$  in concentrated solution (Hugh Marshall). The persulphuric acid, formed by the union of the negative ions in pairs, undergoes double decomposition with the excess of sodium bisulphate, and the less soluble sodium persulphate  $\text{Na}_2\text{S}_2\text{O}_8$  crystallizes out. The other salts are made by double decomposition from this one.

The persulphates decompose readily when heated, yielding pyrosulphates and oxygen:

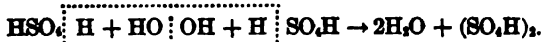


The solution of the acid is an active oxidizing agent:



**Polythionic Acids.** — Di-, tri-, tetra-, and pentathionic acid (p. 431) are all formed simultaneously (along with free sulphur) when sulphur dioxide and hydrogen sulphide gases are passed alternately

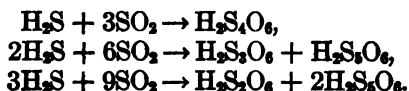
\* This action and the next are not classifiable under any of the ten kinds formerly discussed (p. 228). They consist in the union of H and OH to form water:



Neutralizations (p. 387) they are not, because the interacting substances are both acids. Just as the loss of water from one acid gives an anhydride, so here, the loss of water between two acids gives a mixed anhydride (see Chlorosulphuric acid, below).



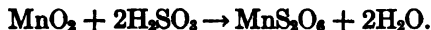
into water, although the gases themselves (p. 416) interact to produce simply free sulphur and water:



Most of these acids and their salts are of minor interest and need not be discussed.

The production of sodium tetrathionate by the action of iodine upon sodium thiosulphate has already been mentioned (p. 448).

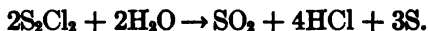
When manganese dioxide is treated with cold sulphurous acid, it interacts rapidly and a solution of manganous dithionate is obtained:



The salts of these acids are in many cases fairly stable, but the acids themselves decompose readily when set free.

#### COMPOUNDS OF SULPHUR WITH CHLORINE AND FLUORINE

**Sulphur Monochloride  $\text{S}_2\text{Cl}_2$ .**—When chlorine gas is passed over heated sulphur it is absorbed, and a reddish-yellow liquid boiling at  $138^\circ$ , is obtained. The molecular weight of this substance as shown by the density of its vapor, indicates that it possesses the formula  $\text{S}_2\text{Cl}_2$ . When thrown into water it is rapidly hydrolyzed producing sulphur dioxide and free sulphur:



Sulphur itself dissolves very freely in the monochloride. The monochloride is employed in vulcanizing rubber.

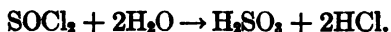
By surrounding sulphur monochloride with a freezing mixture and treating it with excess of chlorine, a liquid dichloride  $\text{SCl}_2$ , and tetrachloride  $\text{SCl}_4$  can be formed. Both are unstable. Moissan prepared sulphur hexafluoride  $\text{SF}_6$ , which is a gas at room temperature (b.p.  $-50^\circ$ ). Unlike the chloride, it is not hydrolyzed by water.

**Thionyl Chloride  $\text{SOCl}_2$ .**—By the action of sulphur dioxide gas upon phosphorus pentachloride, part of the oxygen in the former is replaced by chlorine:

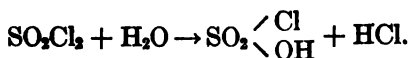


The products are thionyl chloride and phosphorus oxychloride. The

former is a colorless liquid, boiling at  $78^{\circ}$ , and is separated from the latter (b.-p.  $107^{\circ}$ ) by fractional distillation (see Petroleum). It is decomposed immediately on contact with water:



**Sulphuryl Chloride  $\text{SO}_2\text{Cl}_2$ .**—Sulphur dioxide and chlorine gases unite when exposed to direct sunlight to form a liquid known as sulphuryl chloride  $\text{SO}_2\text{Cl}_2$ . When camphor is introduced into the vessel the union takes place much more rapidly, owing to some catalytic effect of this substance. The compound is a colorless liquid, boiling at  $69^{\circ}$ . With water it gives sulphuric acid and hydrogen chloride (p. 443). When a strictly limited amount of water is supplied partial action of the same nature occurs, and the product is known as chlorosulphuric acid:



This intermediate compound may be formed also by the addition of hydrogen chloride to sulphur trioxide.

**Exercises.**—1. What ground is there for assigning the formula  $\text{O}_3$  instead of  $\text{S}_2\text{O}_4$  to sulphur dioxide (p. 427)?

2. Explain why nitric acid is completely displaced by the action of sulphuric acid on sodium nitrate (p. 436).

3. How many times, on an average, does a molecule of nitrous anhydride go through the cycle of changes by which sulphuric acid is produced before it is eliminated in some other form (p. 436)?

4. Make a list of, and classify, the various applications of sulphuric acid to the liberation of other acids.

5. Formulate the behavior of the hydrosulphate-ion (p. 439) when a solution of barium chloride is added to a rather concentrated solution of sulphuric acid.

6. Can you give any reasons for preferring to regard  $\text{KHSO}_4$ , and substances like it, as acid salts rather than double salts of the form  $\text{K}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$  (p. 401)?

7. From a consideration of the facts given in the text, and of the physical conditions, account for the fact that hyposulphurous acid is oxidized by free oxygen first to sulphurous acid and then to sulphuric acid (p. 443), while moist free sulphur, even with oxidizing agents, gives sulphuric acid directly (p. 445)?

8. Why were not pyrosulphuric acid and monopersulphuric acid placed in the list on p. 431 (*cf.* p. 487)?

9. Write in ionic form the equation for the interaction of sodium thiosulphate and iodine in aqueous solution.

10. Restate the import of the following sentence in terms of experimental facts: Liquefied sulphur dioxide "ionizes substance dissolved in it as well as does water" (p. 427).

11. What are the relative volumes, (a) of sulphur dioxide and nitrogen (p. 9) resulting from the roasting of pyrite (p. 424), (b) of air and sulphur dioxide in making sulphuric acid?

12. Assign to the proper classes of ionic actions (pp. 402-406), (a) the action of iodine on sulphurous acid (p. 445), (b) of sulphuric acid on sodium sulphite (p. 447), (c) the ways of forming persulphuric acid (pp. 448-449).

## CHAPTER XXII

### SELENIUM AND TELLURIUM. THE CLASSIFICATION OF THE ELEMENTS

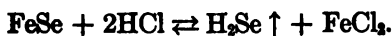
ALONG with sulphur, chemists group two other elements, selenium (Se, at. wt. 79.2) and tellurium (Te, at. wt. 127.5). If the nature of the chief compounds of sulphur is kept in mind, the close analogy between the nature and chemical behavior of the three elements and their corresponding compounds will be noticed at once (see Chemical relations of the sulphur family, below).

#### SELENIUM Se

**Occurrence and Properties of the Element.** — Selenium (Gk. *σεληνη*, the moon) occurs free in some specimens of native sulphur, and in combination often takes the place of a small part of the sulphur in pyrite  $\text{FeS}_2$  (Berzelius, 1817). It is found free in the dust-flues of the pyrite-burners of sulphuric acid works. The familiar forms are, the red precipitated variety, which is amorphous and soluble in carbon disulphide, and the lead-gray, semi-metallic variety, obtained by slow cooling of melted selenium, which is insoluble, and melts at  $217^\circ$ . In the latter form it has some capacity for conducting electricity, which is greatly increased by exposure to light in proportion to the intensity of the illumination. A photometer, using this property, has been devised by Joel Stebbins (1914), for measuring the relative intensity of the light of different stars. Selenium boils at  $688^\circ$ , and at high temperatures has a vapor density corresponding to the formula  $\text{Se}_2$ .

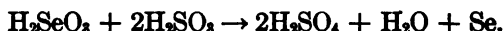
The element unites directly with many metals, burns in oxygen to form selenium dioxide, and unites vigorously with chlorine. It is used in glass-making.

**Hydrogen Selenide.** — Ferrous selenide, made by heating iron filings with selenium, when treated with concentrated hydrochloric acid gives hydrogen selenide:

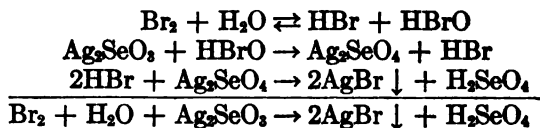


The compound is a poisonous gas, which possesses an odor recalling rotten horse-radish, and is soluble in water. The solution is faintly acid in reaction, and deposits selenium when exposed to the action of the air (*cf.* p. 417). The gas dissociates when heated (*cf.* p. 415). Other selenides, which, with the exception of those of potassium and sodium, are insoluble in water, may be precipitated by leading the gas into solutions of soluble salts of appropriate metals (*cf.* p. 421).

**Selenium Dioxide and Selenious Acid.**—The dioxide  $\text{SeO}_2$  is a solid body formed by burning selenium or evaporating a solution of selenious acid  $\text{H}_2\text{SeO}_3$ . The latter may be made by dissolving the dioxide in hot water, or by oxidizing selenium with boiling nitric acid or *aqua regia* (*q.v.*). Unlike sulphur (p. 414), the element gives little of the higher acid  $\text{H}_2\text{SeO}_4$  by this treatment. In aqueous solution the acid is easily reduced, even by sulphurous acid, to selenium:



**Selenic Acid.**—No trioxide is known. Selenic acid  $\text{H}_2\text{SeO}_4$ , a white solid, is made in solution by oxidizing silver selenite with bromine-water (which contains hypobromous acid, *cf.* p. 223) and filtering:



It is itself a powerful oxidizing agent and, even in dilute solution, liberates chlorine from hydrochloric acid:  $\text{H}_2\text{SeO}_4 + 2\text{HCl} \rightarrow \text{H}_2\text{SeO}_3 + \text{H}_2\text{O} + \text{Cl}_2$ . Sulphuric acid (*cf.* p. 438), on the other hand, is an oxidizing agent only in somewhat concentrated form, and even then it can oxidize hydrobromic acid (p. 272), but not hydrochloric acid.

**Chlorides of Selenium.**—The chlorides are formed by direct union of the elements. The tetrachloride, a yellow crystalline substance, is formed when the monochloride is heated:  $2\text{Se}_2\text{Cl}_2 \rightarrow 3\text{Se} + \text{SeCl}_4$ , the behavior in the case of sulphur chlorides being just the inverse of this (p. 450).

## TELLURIUM Te

Tellurium (Lat. *tellus*, the earth) occurs in sylvanite in combination with gold and silver. It is a white, metallic, crystalline substance, melting at  $452^{\circ}$  (b.-p.  $1400^{\circ}$ ). When formed by precipitation it is a black powder. It conducts electricity to some extent. The vapor density corresponds to the formula  $\text{Te}_2$ . The free element unites with metals directly, and burns in air to form the dioxide.

**Hydrogen telluride**  $\text{H}_2\text{Te}$  is made by the action of acids on metallic tellurides, and its aqueous solution is rapidly oxidized by air with precipitation of tellurium. The tellurides of the alkali metals are soluble in water, the others are insoluble.

**Tellurous acid**  $\text{H}_2\text{TeO}_3$  is formed by oxidizing the element with nitric acid, and is a crystalline solid, little soluble in water. It is a feeble acid, of which many salts have been made. It is also somewhat basic, a sulphate  $2\text{TeO}_2 \cdot \text{SO}_3$  and a nitrate  $\text{Te}_2\text{O}_3(\text{OH})\text{NO}_3$  being known. In this respect it differs markedly from sulphurous acid.

**Telluric acid** is made by oxidizing tellurous acid in aqueous solution with chromic acid (p. 418). It is difficultly soluble in water. It does not affect indicators, and is therefore actually more feebly acidic than is hydrogen sulphide. It is obtained as a solid having the composition  $\text{H}_6\text{TeO}_6$  (or  $3\text{H}_2\text{O} \cdot \text{TeO}_3$ ) on evaporating the solution. When heated, this body loses water, some of the **trioxide**  $\text{TeO}_3$  being formed. The last is a yellow solid, which shows no tendency to recombine with water, in this respect resembling silica (*q.v.*). Tellurates of the alkali metals may be made by heating the tellurites with potassium or sodium nitrate:  $\text{K}_2\text{TeO}_3 + \text{KNO}_3 \rightarrow \text{K}_2\text{TeO}_4 + \text{KNO}_2$ .

Tellurium forms two very stable chlorides,  $\text{TeCl}_2$  and  $\text{TeCl}_4$ , which are decomposed by water. The second, however, exists in solution with excess of hydrogen chloride:  $\text{TeCl}_4 + 3\text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{TeO}_3 + 4\text{HCl}$ , showing the tellurous acid to be basic in properties and the element tellurium to be, to a certain degree, a metallic element (see Chap. XXXII).

We have now a means of deciding whether a substance containing the elements of water, such as, for example, telluric acid, should be written,  $\text{H}_6\text{TeO}_6$ , or as a hydrate  $\text{H}_2\text{TeO}_3 \cdot 2\text{H}_2\text{O}$ . Baker and Adam have shown that plates made of true hydrates are permeable by water vapor, but that crystals of anhydrous substances, such as cupric sulphate, are not so permeable. They found that crystals of telluric acid are not permeable by water vapor, so that  $\text{H}_6\text{TeO}_6$  is the correct formula.

**The Chemical Relations of the Sulphur Family.**— It will be seen that sulphur, selenium, and tellurium are bivalent elements when combined with hydrogen or metals. In combination with oxygen they form unsaturated compounds of the form  $X^{IV}O_2$ , while their highest valence is found in  $SO_3$ ,  $TeO_3$ , and  $H_2SeO_4$ , where they must be sexivalent. The general behavior of corresponding compounds is very similar. At the same time, there is in all cases a progressive change as we proceed from sulphur through selenium to tellurium. The elementary substances themselves, for example, become more like metals, physically, and they show higher and higher melting-points. The affinity for hydrogen decreases, as is shown by the increasing ease with which the compounds  $H_2X$  are oxidized in air. The affinity for oxygen likewise decreases, for the elements become increasingly difficult to raise to the highest state of oxidation. On the other hand, the tendency to form higher chlorides becomes greater. We note also that the compounds  $H_2XO_4$  become less and less active as acids, and a distinct basic tendency begins to assert itself.

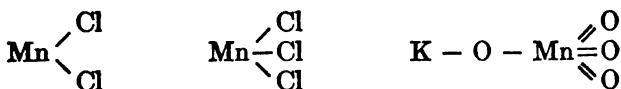
### THE PERIODIC SYSTEM

Classification, or the arrangement of facts on the basis of likeness, is part of the method of science. In chemistry the multitude of facts is not less than in other sciences, and the necessity of arrangement equally urgent. It is needed to make possible the systematic description of the ascertained facts, and to furnish a guide in investigation, by suggesting stochastic hypotheses (p. 176), and so pointing out directions in which new facts of interest may be found. Thus, as an aid to memory, we have treated the halogens as one family and S, Se, and Te as another. In each case, we have presented the properties common to all members of the group, and have then pointed out the differences. Again, in investigation, as soon as we have discovered that sulphur and selenium are allied elements, we realize the direction in which fruitful results may be expected, and we proceed to make the corresponding compounds and to note the resemblances and differences in the conditions for preparation and in the properties of the compounds obtained.

At first sight, the most definite method of classification would appear to be the grouping of elements of like valence. But this brings together sodium and chlorine—an element whose hydrogen compound is unstable and without markedly characteristic properties,

and whose hydroxyl compound is an active base, with an element whose hydrogen compound is an active acid and whose hydroxyl compound is, in a feeble degree, an acid also. This method homologates similar and contrasting elements indiscriminately.

**Metallic and Non-Metallic Elements.**—Thus far we have found the division into metallic and non-metallic elements very serviceable for classification in terms of chemical relations (p. 150). This distinction we shall continue to employ. **The metallic, or positive elements** (p. 357), (1) form positive radicals and ions containing no other element (*cf.* p. 375). Thus the metals give sulphates, nitrates, carbonates, and other salts, which furnish a metallic ion, such as  $\text{Na}^+$  or  $\text{K}^+$ , together with the ions  $\text{SO}_4^-$ ,  $\text{NO}_3^-$ , and  $\text{CO}_3^-$ . (2) Their hydroxides,  $\text{KOH}$ ,  $\text{Ca}(\text{OH})_2$ , etc., give the same metallic ion, and the rest of the molecule forms hydroxide-ion. That is to say, their hydroxides are bases and their oxides are basic. The metallic elements often enter, but only *with other elements*, into the composition of a negative ion, as is the case with manganese in  $\text{K.MnO}_4$ , with chromium in  $\text{K}_2\text{Cr}_2\text{O}_7$ , and with silver in  $\text{K.Ag}(\text{CN})_2$ .\* But the most definitely metallic elements form with oxygen such a negative ion only while exhibiting a *different valence* from that which they possess when acting as positive elements. Thus, manganese when a positive element has the valences two and three,  $\text{MnO}$  and  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn.Cl}_2$  and  $\text{Mn.Cl}_3$ ,  $\text{Mn.SO}_4$  and  $\text{Mn}_2(\text{SO}_4)_3$ , etc., while in permanganates we have potentially the oxide  $\text{Mn}_2\text{O}_7$ , ( $\text{K}_2\text{O.Mn}_2\text{O}_7 = 2\text{KMnO}_4$ ), in which it is septivalent. The graphic formulæ express the difference in valence:



If we knew only the compounds in which manganese is septivalent, we should regard it as a non-metallic element pure and simple, the metallic appearance of the free element to the contrary notwithstanding.

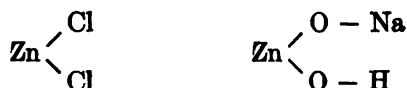
**The non-metallic or negative elements**, (1) are found chiefly in negative radicals and ions. They form no nitrates, sulphates, carbonates, etc., for they could not do so without themselves alone constituting the positive ion. We have no such salts of oxygen, sulphur,

\* The mode of division into ions is shown by the position of the period in the formula.



carbon, or phosphorus, for example. (2) Their hydroxides, although their formulæ may be written  $\text{ClO}_2\text{OH}$ ,  $\text{P}(\text{OH})_3$ ,  $\text{SO}_2(\text{OH})_2$ , furnish no hydroxide ions, as this would involve the same consequence. These hydroxides are divided by dissociation, in fact, so that the non-metal forms part of a compound negative radical, and the other ion is hydrogen-ion,  $\text{ClO}_2\text{H}$ ,  $\text{PO}_3\text{H.H}_2$ ,  $\text{SO}_4\text{H}_2$ . (3) Their halogen compounds, like  $\text{PCl}_3$  (p. 210) and  $\text{S}_2\text{Cl}_2$  (p. 450), are completely hydrolyzed by water, and the actions are not, in general, reversible. The halides of the *typical* metals are not hydrolyzed (see Chap. XXXII), and with those that are not typical, the action is reversible.

The distinctions are not perfectly sharp, however. Thus, zinc (*q.v.*) gives both salts like the sulphate  $\text{Zn.SO}_4$  and chloride  $\text{Zn.Cl}_2$ , and compounds like sodium zincate (p. 122)  $\text{ZnO}_2\text{H.Na}$ , showing the same valence in both classes:



Its hydroxide ionizes in two ways,  $\text{Zn}(\text{OH})_2$  and  $\text{ZnO}_2\text{H.H}$ . Similarly telluric acid  $\text{H}_2\text{TeO}_3$  acts both as acid and base (p. 455). We shall find this double behavior conspicuous in the compounds of arsenic and antimony. In spite of the partial merging of the two classes of elements, however, the general distinction is worth preserving (see Chap. XXXII).

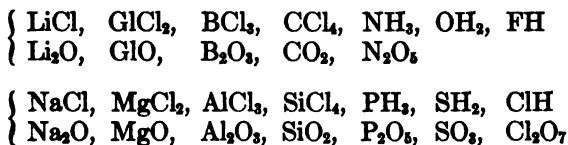
**Classification by Atomic Weights.**—A closer discrimination than that furnished by these two categories is required, however, and a study of the order into which the elements fall when arranged according to their atomic weights has provided this to some extent.

The first indication of a significant relation between the atomic weights and the properties of the elements was given by a fact noted by Döbereiner (1829). He drew attention to the existence of closely similar elements in sets of three (*triads*), where the central element was intermediate in properties between the two others, and the atomic weight of the central element was almost the exact arithmetical mean of the weights of the other two. The three following triads illustrate this relation:

Chlorine . . . . .	35.46	Sulphur . . . . .	32.06	Calcium . . . . .	40.07
Bromine . . . . .	79.92	Selenium . . . . .	79.2	Strontium . . . . .	87.63
Iodine . . . . .	126.92	Tellurium . . . . .	127.5	Barium . . . . .	137.37
Mean of Cl and I,	81.2	Mean of S and Te,	79.8	Mean of Ca and Ba,	88.7

Newlands (1863-4) discovered a surprising regularity when the elements were placed in the order of ascending atomic weight. Omitting hydrogen (at. wt. 1) the first seven are: lithium (7), glucinum (9), boron (11), carbon (12), nitrogen (14), oxygen (16), fluorine (19). These are all of totally different classes, and include first a metal forming a strongly basic hydroxide, then a metal of the less active sort, then five non-metals of increasingly negative character, the last being the most active non-metal known. The next element after fluorine (19) is sodium (23), which brings us back sharply to the elements that form strongly basic hydroxides. Omitting none, the next seven elements are: sodium (23), magnesium (24.3), aluminium (27), silicon (28.3), phosphorus (31), sulphur (32), chlorine (35.5). In this series there are three metals of diminishing positiveness, followed by four non-metals of increasing negative activity, the last being a halogen very like fluorine. On account of the fact that each element resembles most closely the eighth element beyond or before it in the list, the relation was called the *law of octaves*. After chlorine the octaves become less easy to trace. Potassium (39) follows chlorine and corresponds satisfactorily to sodium, but it is not until seventeen successive elements have been set down that we reach one closely resembling chlorine, namely, bromine.

That this periodicity in chemical nature is more than a coincidence is shown by the fact that the valence and even the physical properties, such as the density, show a similar fluctuation in each series, and recurrence in the following one. In the first two series the compounds with other elements are of the types:



Thus the valence towards chlorine or hydrogen ascends to four and then reverts to one in each octave. The highest valence, shown in oxygen compounds, ascends from lithium to nitrogen with values one to five, and then fails because compounds are lacking. In the second octave, however, it goes up continuously from one to seven.

Again, the densities of the elements in the second series, using the data for red phosphorus and liquid chlorine, are:

Na 0.97, Mg 1.75, Al 2.67, Si 2.49, P 2.14, S 2.06, Cl 1.33.

Of greater significance chemically are the related numbers representing the volumes in cubic centimeters occupied by a gram-atomic weight of each element (the **atomic volumes**):

Na 24, Mg 14, Al 10, Si 11, P 14, S 16, Cl 27.

A similar regular fluctuation is shown by all the physical properties of corresponding compounds.

**Mendelejeff's Scheme.**— In 1869 Mendelejeff published an important contribution towards adjusting the difficulty which the elements following chlorine presented, and developed the whole conception so completely that the resulting system of classification has been connected with his name ever since. Almost simultaneously Lothar Meyer made similar suggestions, but did not urge them with the same conviction or elaborate them so fully. The following table, in which the atomic weights are expressed in round numbers, is a modification of one of Mendelejeff's.

The chief change from the arrangement in simple octaves is that the third series, beginning with potassium, is made to furnish material for two octaves, potassium to manganese and copper to bromine, and is called a **long series**. The valences fall in with this plan fairly well. Copper, while usually bivalent, forms also a series of compounds in which it appears to be univalent. Iron, cobalt, and nickel cannot be accommodated in either octave, as their valences are always two or three, so these elements are set off in a column by themselves. At the time Mendelejeff made the table, three places in the third (long) series had to be left blank, as a trivalent element [Sc] was lacking in the first octave, and a trivalent [Ga] and a quadrivalent one [Ge] in the second. These places have since been filled, as we shall presently see. The first two (the *short*) series have been split in the table, as lithium and sodium closely resemble potassium, while the remaining members of these series fall more naturally over the corresponding elements of the second octave of the third series.

The fourth series (long) is nearly complete. It begins with an active alkali metal, rubidium, and ends with iodine, a halogen. The rule of valence is strictly preserved throughout the series, and in general the elements fall below those which they most closely resemble.

The fifth, sixth, and seventh (long) series are incomplete, but the order of the atomic weights and the valence enables us satisfactorily to place many of the elements. The chemical relations to elements

# ONE OF MENDELEJEFF'S TABLES, MODIFIED

[illegible]

Between cerium (140) and tantalum (183) there are twelve rare elements (see p. 470). These elements, however, do not fit into the series, because their valences and other chemical properties do not permit most of them to be distributed over so many different groups.

of the fourth series justify the position assigned to each. Caesium, for example, is the most active of the alkali metals; barium has always been classed with strontium, and bismuth with antimony. There are, however, about twelve more or less rare elements which cannot easily be fitted into the vacant places.

In two cases a slight displacement of the order according to atomic weights was necessary. Cobalt was put before nickel because it resembled iron more closely, although the atomic weights are in the opposite order. Tellurium and iodine are placed in that order to bring them into the sulphur and halogen groups, respectively. Their valences and other chemical relations both require this. The general agreement, however, is very remarkable.

**General Relations in the System.**—In every octave the **valence** towards oxygen ascends from one to seven, while that towards hydrogen, in the cases of the four last elements (when they combine with hydrogen at all), descends from four to one. The **atomic volume** disregards the subsidiary octaves in the long series. It descends towards the middle of each series (long or short), and ascends again towards its initial value. The other **physical properties** fluctuate within the limits of each series in a similar way. The values of each physical constant for corresponding members of the **successive series** do not exactly coincide, however. A progressive change, as we descend each vertical column, is the rule. Thus the densities of the alkali metals rise from lithium (0.53) to caesium (1.87). In the same group the melting-points descend from lithium (186°) to caesium (26.5°).

It must be stated that no mathematical (quantitative) relation between the values for any property and the values of the atomic weights has been discovered; only a general (quantitative) relationship can be traced. Anticipating the discovery of some more exact mode of stating the relationship in each case, and remembering that similar values of each property recur *periodically*, usually at intervals corresponding to the length of an octave or series, the principle which is assumed to underlie the whole, the **periodic law**, is stated thus: **All the properties of the elements are periodic functions of their atomic weights.**

That the **chemical relations** of the elements vary just as do the physical properties of the simple substances is easily shown. Thus, each series begins with an active metallic (positive) element, and ends with an active non-metallic (negative) element, the intervening

elements showing a more or less continuous variation between these limits. Again, the elements at the top are the least metallic of their respective columns. As we descend, the members of each group are more markedly metallic (in the first columns), or, what is the same thing, less markedly non-metallic (in the later columns; cf. p. 455).

In the first series boron is the first non-metallic element we encounter. In the second series silicon is the first such element. In the third there is more difficulty in deciding. Titanium, vanadium, and germanium are usually, though with questionable propriety, classed as metallic elements.\* Selenium is undoubtedly a non-metallic element. Arsenic is, on the whole, a non-metallic element. In the fourth series tellurium is commonly considered to be the first non-metallic element. Thus a zigzag line, shown in the table, separates all the non-metallic elements from the rest of the elements, and confines them in the right-hand upper corner.

A more compact form of the table, also based upon one of Mendelejeff's, is printed at the end of this book, opposite the rear cover. The only difference between this and the other is that the two octaves of each long series have been placed in the same set of seven main columns. The irregular sets of three elements, consisting of the iron, palladium, and platinum groups, occupy a column on the right of the main columns, and are often called collectively the **eighth group**. The recently discovered noble gases, found chiefly in the air, have been placed at the left-hand side. Since they do not enter into combination at all, their valence may appropriately be given as zero. With the exception of argon, the values of their atomic weights agree well with this assignment. Hydrogen is the only common element whose place is still in debate. Many rare elements have also been omitted, and tantalum has been placed immediately after cerium. The valence is shown by the general formula at the head of each column.

**Chemical Relations and the Periodic System.**—It is so easy to confuse the qualities which enable us to place an element in a suitable group or family, with those which are of no service in this respect, although they may be used to justify the assignment **after it has been made**, that it seems best to give a concrete illustration, with the halogen family as the example. In the follow-

\* In discussing chemical relations, the term **metallic element** is preferable to **metal**. The free element (*e.g.*, arsenic) may have the luster of a metal, and yet the element, in combination, may be non-metallic or negative.

ing table there are named: (1) a few specific physical properties of a simple uncombined substance, (2) a few chemical properties of a simple uncombined substance, (3) the chemical relations of the element as judged by its properties when in combination, or by the behavior of its compounds:

Phys. Props. of Simple Substance		Chem. Props.	Chem. Relations of Element.
Color		Molar wt.	Atomic Wt.
Density		Combines with	Valence
Crit. temp.		.....	Metallic or non-metallic element
M.-p., b.-p.		Displaces	.....
Loses these after combination			Possesses these in combination
Could not group elements by these properties			Do group the element by these relations

Might oxygen fairly be included in the halogen family? It is almost colorless, so it might be the first member of the family, iodine, the most strongly colored, being the last. Its density is lower than that of any halogen, as are also its critical temperature, boiling-point, and melting-point. We cannot decide on the basis of physical properties alone. Or, using the properties in the second column, can we ascertain whether sulphur might fairly be considered a halogen? Its molar weight is 256, higher than that of iodine, although like iodine, it gives lower values at higher temperatures, so it might be the last member of the family. It combines directly with practically all the metals, just as do the halogens. All the halogens displace it from combination with metals. It unites directly, and vigorously with oxygen, while iodine forms more stable compounds with oxygen than do bromine or chlorine. The last two facts would then place sulphur as last member of the series. But, should it be in this family at all? The chemical properties of the simple substances do not enable us to decide.

When we examine the column of chemical relations, however, we find oxygen to be bivalent, while the halogens are univalent (and septivalent towards oxygen), so oxygen does not belong to this group. Again, sulphur is non-metallic (oxides acidic, halides hydrolyzed completely), just like the halogens. But sulphur is bivalent or sexivalent, and its atomic weight places it between fluorine and chlorine, and not after iodine, so that it cannot be included in this

group. Thus, it is evident that we decide which elements form a coherent family by consideration of the chemical relations, *i.e.*, by the qualities each element shows while in combination.

**Applications of the Periodic System.** — The system has found application chiefly in four ways:

1. In the **prediction of new elements**. Mendelejeff (1871) drew attention to the blank then existing between calcium (40) and titanium (48). He predicted that an element to fit this place would have an atomic weight 44 and would be trivalent. From the nature of the surrounding elements, he very cleverly deduced many of the physical and chemical properties of the unknown element and of its compounds. He named it eka-boron (Skr. *eka*, one). In 1879 Nilson discovered scandium (44), and its behavior corresponded closely with that predicted for eka-boron. Mendelejeff also described accurately two other elements, likewise unknown at the time. They were to occupy vacant places between zinc and arsenic, and were named eka-aluminium and eka-silicon. In 1875 Lecoque de Boisbaudran found gallium, and in 1888 Winkler discovered germanium, and these blanks were filled. Other possible elements, such as eka-manganese, were described, but still remain to be discovered.

2. By enabling us to decide on **correct values for the atomic weights** of some elements, when the equivalent weights have been measured, but no volatile compound is known (*cf.* p. 63, 239). Thus the atomic weight of uranium was thought to be 120 until it was observed that no place near to antimony (120) remained unoccupied. With the value 240 (now 238.2), the element was accommodated at the foot of the column containing those which it most resembled. Again, the equivalent weight of indium was 38 and, as the element was supposed to be bivalent, it received the atomic weight 76. It was quite out of place near arsenic (75), however, being decidedly a metallic element. As a trivalent element with the atomic weight 115, it fell between cadmium and tin. Later work fully justified the change. Still again, glucinum, with equivalent weight 4.5, resembled aluminium so strongly that it was thought to be trivalent, like that element, and to have the atomic weight 13.5. But the only vacancy in the first series then existing was between lithium (7) and boron (11) and subsequent investigation showed that the properties of glucinum placed it most fittingly in that position as a bivalent metallic element with the atomic weight 9. Recently, radium (*q.v.*) has been discovered, and found to have the equivalent weight 113 and to resemble



barium. If, like barium, it is bivalent, it occupies a place under this element, in the last series. The atomic weights of cobalt and nickel, and of tellurium and iodine, however, cannot be adjusted.]

3. By **suggesting problems for investigation**. The periodic system has been of constant service in the course of inorganic research, and has often furnished the original stimulus to such work as well. For example, the atomic weights of the platinum metals at first placed them in the order, Ir (197), Pt (198), Os (199), although the resemblance of osmium to iron and ruthenium would have led us to expect that this element should come first. For similar reasons platinum should have come last, under palladium. A reinvestigation of the atomic weights, suggested by these considerations, was undertaken by Seubert, and the old values were found in fact to be very inaccurate. He obtained: Os = 191, Ir = 193, Pt = 195.

Again, the atomic weight of tellurium bore the value 128, when the table was first constructed, and it was confidently expected that re-examination would bring this value below that of iodine (then 127, now 126.92). Several most careful studies of the subject have been made, using different methods. It seems probable that the real value of the atomic weight is not far from Te = 127.5, and therefore more than half a unit greater than that of iodine. Since, however, quantitative correspondence is found nowhere in the system, the existence of marked inconsistencies like this need not shake our confidence in its value when it is used with due consideration of the degree of correspondence to be expected.

Originally lead, although it fell in the fourth column, possessed only one compound,  $\text{PbO}_2$ , in which it seemed to be undoubtedly quadrivalent. Search for salts of the same form, however, speedily yielded the tetrachloride  $\text{PbCl}_4$ , tetracetate, and many others. The existence of osmic acid  $\text{OsO}_4$ , and a corresponding compound of ruthenium, suggests that other compounds of the elements of the eighth group, displaying the valence eight, may be capable of preparation. The collocation of copper, silver, and gold, in the same column with the alkali metals, is not at present perfectly satisfactory, and suggests the advisability of strengthening their position, if possible, by further investigation.

In the same way, incorrect values of many physical properties have been detected, and have been rectified by more careful work.

4. By furnishing a **comprehensive classification of the elements**, arranging them so as to exhibit the relationships among the physical

and chemical properties of the elements themselves and of their compounds. Constant use will be made of this property of the table in the succeeding chapters. Having disposed of the halogen and sulphur families (excepting the oxygen compounds of the former), situated, respectively, in the seventh and sixth columns of the table (at the end of this book), we shall presently take up nitrogen and phosphorus from the right side of the fifth column. Then from the fourth column, we shall select carbon and silicon, and from the third boron, leaving the other more decidedly metallic elements for later treatment.

***Inadequacy of the Periodic System.***—The periodic system is often described as if it furnished a classification of the properties of chemical substances which was complete in its scope, and ideal in its exactness. This, however, is far from being the case.

The **order of activity** (E. M. Series) of the metals (pp. 129, 404) and of the non-metals (p. 284) summarizes many properties, and explains many features of the chemical behavior of the elements. This list is scattered through the periodic table (compare both), without any trace of regularity. The **order of solubility of the sulphides**, a valuable property in qualitative analysis, is practically coincident with the E. M. series (see under Cadmium), and is not to be found in the periodic system.

The periodic system concentrates attention too largely on **one of the valences of each element**. Thus, for manganese, it focuses attention on the septivalent form in the permanganates. But manganous salts are more like the ferrous, the cobaltous, the chromous, and other sets of salts, none of which are in the same column of the table. Similarly, the manganic salts are like the ferric salts and the salts of aluminium. Again, copper is univalent in one series of salts, but in its better known salts it is bivalent. Silver, which belongs to the same periodic family is always univalent, while gold, also in the same family, is univalent or trivalent, and in the latter case is almost wholly a non-metallic element. Indium has three sets of salts, and similar remarks could be made about it and about the very many other multivalent elements. If it were possible to place each element in several different columns, one for each of the valences that it shows, the table would then include far more of the properties of the elements. But this cannot be done, for, according to the order of magnitude of the atomic weights, there is but one place for each element. In other words, the periodic system largely

ignores the variety of *different* classes of chemical relations which an element with several valences always shows.

Attention has also been called to about **twelve rare elements** for which suitable positions cannot be found amongst the vacant places in the table. Then, also, the **physical properties** of elements and compounds follow the order of the elements in a family in a general way. But no formula can be devised by which the properties can be calculated from the atomic weight and other independent data. Often, one or two physical properties do not even follow the order of the elements in the family. The values of the physical properties, the number and kinds of valences, and so forth, could be predicted from the table only in a general way, and sometimes the prediction would be entirely false. The curve obtained when the atomic volumes are plotted against the atomic weights follows the different series with surprising regularity, but atomic volumes cannot be used in analysis, or in most kinds of chemical work, and therefore lack practical value.

These remarks are made, merely to guard against the supposition that anything like a complete account of chemistry can be extracted from the periodic system. This system can be used, and we shall use it where it is of value, but we must not allow the science to be distorted or emasculated by ignoring the important relations of which the system takes no notice.

### THE ATOMIC NUMBERS

When the water of hydration escapes as vapor from a hydrate, the crystals frequently crumble to dust (p. 154). There are, however, interesting exceptions. Minerals of the zeolite class, for example, can be deprived of water without losing their coherence. When the desiccated specimen is placed in contact with water vapor at a sufficient pressure, the water molecules re-enter the crystal and the original hydrate is recovered. More remarkable still is the fact that, instead of water vapor, gases like hydrogen sulphide, ammonia, carbon dioxide, and alcohol vapor can be used, and enter the crystal taking the place of the water (see Permutite). These substances are chemically so different from water, and from one another, that the phenomenon looks more like a physical substitution than a replacement in chemical combination. These and other facts suggest that hydrates may be crystallographic arrangements of different kinds of particles, of a physical nature, rather than chemical com-

pounds in the ordinary sense. This suspicion has recently been confirmed in a remarkable way.

**Moseley's Atomic Numbers.**—We have seen that simple, mathematical relations between the atomic weights and the physical or chemical properties of an element do not exist. In several instances, the atomic weights are not even in the same order as are the values of the properties. We have now obtained from another direction numbers which seem to be more fundamental even than atomic weights.

Visible light, X-rays, and wireless electric waves are all vibrations of the same nature in the ether. They differ only in wave-length, the order of the wave-lengths being  $10^{-6}$  cm.,  $10^{-8}$  cm., and  $10^5$  cm. (10 kilometers), respectively. Now, just as the spectrum of visible light is obtained by using a grating, on which the rulings are separated by distances of the order of the wave-length of such light, so ordinary crystals give spectra of X-rays, because they are composed of particles arranged in rows about one thousand times closer and so form a suitable grating for X-rays. This fact was first discovered by Dr. Laue of the University of Zurich (1912). The X-rays are produced in an evacuated tube by cathode rays, which are streams of electrons emanating from the cathode (C, Fig. 113), when they strike the anti-cathode (A).

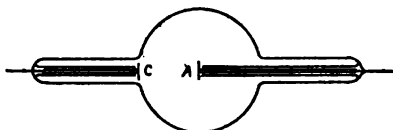


FIG. 113.

With different elements on the anti-cathode, X-rays of slightly different wave-lengths, and giving therefore different X-ray spectra, are produced. By using different elements, Moseley (1914) has found that the higher the atomic weight the shorter the wave-length of the X-rays. When the elements are arranged in the order of these wave-lengths, whole numbers can be assigned to each which are inversely proportional to the square roots of the wave-lengths of corresponding lines in their X-ray spectra. These **atomic numbers** have been determined for most of the elements, the atomic weights of which lie between those of aluminium and gold. In the following table, the atomic numbers for these elements are given and, for the sake of greater completeness, numbers for the twelve elements preceding aluminium have been inserted also.

## ATOMIC NUMBERS (MOSELEY)

H 1	He 2	Li 3	Be 4	B 5	C 6	N 7	O 8	F 9	.....	.....	.....
Ne 10	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	.....	.....	.....	.....
A 18	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	.....
.....	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	.....	.....	.....	.....
Kr 36	Rb 37	Sr 38	Y 39	Zr 40	Cb 41	Mo 42	— 43	Ru 44	Rh 45	Pd 46	.....
.....	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	.....	.....	.....	.....
Xe 54	Cs 55	Ba 56	La 57	Ce 58	Ta 59	W 60	— 61	Os 62	Ir 63	Pt 64	.....
.....	Au 79	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

\* The atomic numbers 59–72 are those of the metals of the rare earths: Pr 59, Nd 60, — 61, Sa 62, Eu 63, Gd 64, Tb 65, Dy 66, Ho 67, Er 68, Tm 69, Yb 70, Lu 71, — 72.

It will be seen that there is a whole number available for every known element, up to and including gold, and not omitting the rare elements which have no satisfactory place in the periodic system. There are two blank numbers in the table which correspond to two spaces below Mn in the periodic system, and two more amongst the rare elements, indicating only four elements with atomic weights less than that of gold yet to be discovered. The atomic numbers of argon and potassium place them in the chemically correct order, while the atomic weights do not. The same is true of tellurium and iodine. Finally, it is evident that the atomic weight of each element is, roughly, double its atomic number.

The atomic numbers represent the number of unit positive charges of electricity in the nucleus of the atom of each element (p. 354). Rutherford has shown that the nucleus contains almost the whole mass of the atom, although one or more electrons (negative) are present also. Thus, the positive nucleus of the hydrogen atom is 1800 times heavier than an electron. The nucleus, however, is very minute, having a diameter only about one-eighteenth hundredth of that of an electron.

The atomic numbers apparently determine all the properties of each element, and are more fundamental than the atomic weights. The latter are secondary properties, in most cases modified by other factors, and in two cases actually thrown out of order by such factors.

**Crystal Structure.**—In this connection it may be mentioned that by using crystals of different substances as X-ray gratings, W. L. Bragg (1914) has been able to measure the distances between the rows of particles in crystals. He also finds that the particles,

the regular arrangement of which gives the structure (p. 171) of the crystal (*e.g.*, a cube of common salt), are not the molecules of the compound, much less aggregates of such molecules, but the atoms of the constituent elements. It would thus appear that the physical forces (if we may call them physical) which hold the crystalline solid together have subordinated the chemical, molecular structure, and have arranged the constituent atoms, as the units of the structure, in a crystallographic pattern. Of course, when the crystal-form is destroyed, by melting, solution, or vaporization, the neighboring atoms remain united in groups, constituting the chemical molecules of the substance.

**Exercises.** — 1. Can you explain the presence of *free* selenium in the flues of pyrite burners (p. 454)?

2. How should you attempt to obtain  $H_2Te$ , and what physical and chemical properties should you expect it to possess?

3. Why does the existence of tellurium tetrachloride in solution in aqueous hydrochloric acid show tellurium to be somewhat metallic in chemical properties?

4. Make a list of bivalent elements and criticize this method of grouping as a means of chemical classification.

5. Write down the symbols of the elements in the fourth series (that beginning with rubidium, and ending with iodine) on p. 461. Record the valence of each element toward oxygen, using for reference the chapters in which the oxygen compounds are described.

## CHAPTER XXIII

### OXIDES AND OXYGEN ACIDS OF THE HALOGENS. OXIDATION AND REDUCTION

THE chief subjects of practical importance touched upon in this chapter are connected with bleaching powder  $\text{CaCl}(\text{OCl})$ , and potassium chlorate  $\text{KClO}_3$  and perchlorate  $\text{KClO}_4$ . Hence our attention will be largely directed to the modes of making these substances and to their relations to one another. Incidentally, we shall encounter many actions of a complex and, to us, more or less novel kind.

**Compounds of Chlorine Containing Oxygen.** — The following are the names and formulæ of the substances:

$\text{HClO}$ Hypochlorous acid	$\text{Cl}_2\text{O}$ Hypochlorous anhydride
$(\text{HClO}_2)$ Chlorous acid	$\text{ClO}_2$ Chlorine dioxide
$\text{HClO}_3$ Chloric acid	$\text{Cl}_2\text{O}_7$ Perchloric anhydride
$\text{HClO}_4$ Perchloric acid	

There are also salts of these acids, like the three substances mentioned in the first paragraph. Chlorous acid is itself unknown, but potassium chlorite  $\text{KClO}_2$  and some other derivatives have been made.

The two anhydrides (p. 150), when brought into contact with water, combine with it to form the acids opposite which they stand in the table. Chlorine dioxide (*q.v.*), however, is not related to any one acid in this way.

All these compounds differ from most that we have hitherto discussed inasmuch as not one of them can be made by direct union of the simple substances.

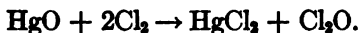
**Nomenclature of the Acids and their Salts.** — The acids and salts are named on a plan similar to that used in the case of the sulphur acids:

KClO Potassium hypochlorite,	HClO Hypochlorous acid,
KClO <sub>2</sub> Potassium chlorite,	HClO <sub>2</sub> Chlorous acid,
KClO <sub>3</sub> Potassium chlorate,	HClO <sub>3</sub> Chloric acid,
KClO <sub>4</sub> Potassium perchlorate.	HClO <sub>4</sub> Perchloric acid.

It should be noted, however, that the use of *ic* and *ous* for more and less oxygen, respectively, and of *hypo* for still less and of *per* for still more oxygen, are simply relative terms *within a single group*. Thus, sulphuric acid H<sub>2</sub>SO<sub>4</sub> has a composition entirely different from chloric acid, and both of these differ in composition from phosphoric acid H<sub>3</sub>PO<sub>4</sub>. The names and formulæ of each group must be learned, separately.

**Chlorine Monoxide or Hypochlorous Anhydride Cl<sub>2</sub>O.**—

A solution of pure hypochlorous acid is most easily prepared by dissolving the anhydride in water. The anhydride is obtained by passing chlorine gas over warmed mercuric oxide\* HgO (Fig. 88, p. 217). Each of the constituents of the oxide combines with chlorine:



The mercuric chloride then unites with another formula-weight of the mercuric oxide to form a solid basic mercuric chloride HgO, HgCl<sub>2</sub>, which remains in the tube. The chlorine monoxide is a brownish-yellow, heavy, easily liquefied gas (b.-p. 5°). Both the gaseous and liquefied forms of it, the former when warmed, the latter when touched by paper or dust, decompose into the constituents with explosion. The gas dissolves in water very easily (200 : 1, by vol.). The yellow solution of hypochlorous acid which results:



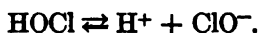
has a strong odor of chlorine monoxide, because the combination is reversible, as it is in sulphurous acid (p. 444). There are other ways of preparing a *dilute* solution of the acid (see below).

**Properties of Hypochlorous Acid.**—1. Hypochlorous acid is *unstable*, and cannot be made, excepting in solution, or kept, excepting in dilute solution. This is in consequence of its tendency to decompose in three different ways, one of which, the liberation of the anhydride, has just been mentioned.

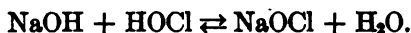
\* The crystalline, red oxide is not sufficiently active. The oxide must be precipitated from sodium hydroxide and mercuric nitrate solutions, it must be washed thoroughly on a filter, and be dried at 300–400° before use.



2. Hypochlorous acid is a little-ionized, **weak acid**.



It neutralizes active bases, its ionization equilibrium being displaced forwards as the hydrogen-ion  $\text{H}^+$  is removed to form water:



3. The solution, if strong, or when boiled, gives off chlorine monoxide  $\text{Cl}_2\text{O}$ , the union with water being reversible.

4. If the solution is concentrated, much of the hypochlorous acid **changes** gradually into **chloric acid** and hydrogen chloride. This is a self-oxidation. It occurs even in the dark:



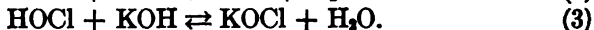
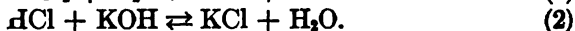
5. When the solution is exposed to **sunlight**, **oxygen is evolved**.



This decomposition always takes place in sunlight, whether the acid is present alone in the water, or along with other substances. We have already noted this fact in discussing chlorine-water (p. 223), which contains this acid.

6. In consequence of the ease with which it gives up oxygen, hypochlorous acid is a strong **oxidising agent**. In this direction it has several important commercial applications (see below).

**Commercial Preparation of Hypochlorites.**—For commercial purposes, pure hypochlorites are not, as a rule, required. Hence, **sodium** or **potassium hypochlorite** is prepared by the action of sodium or potassium hydroxide on chlorine-water. The latter contains both hydrochloric and hypochlorous acids, and so a solution containing a mixture of sodium or potassium chloride and hypochlorite is obtained:

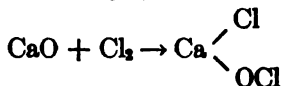


Although action (1) is only partial, being strongly reversible, the neutralization of the two acids in actions (2) and (3) displaces the first equilibrium, and all three actions proceed to completion. Action (1), followed by (2) or (3), is a pair of consecutive actions (p. 445), of which the second (the neutralization) is the speedier of the two. Both pairs of consecutive actions (1) + (2) and (1)

+ (3), can be combined in one equation. Thus, omitting the water, which appears both among products and initial substances and in any case is present in large excess as a solvent, and omitting also the two acids, which are used up as quickly as they are produced by equation (1) and are not amongst the actual products, we get, by addition of the three equations (*cf.* p. 270), the final equation:

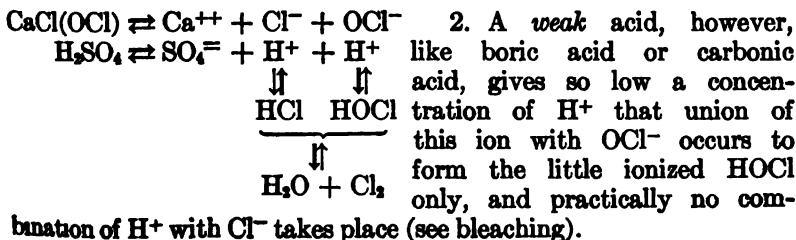


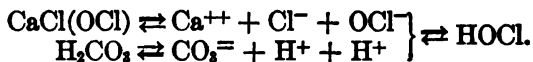
As lime is a less expensive alkali than is potassium or sodium hydroxide, it is largely used. The chlorine is led into rotating cylinders containing quicklime  $\text{CaO}$ :



The product is not a mixture, but a mixed salt (p. 401), known as **bleaching powder** or "chloride of lime." The fact that this is a mixed salt does not interfere with its use as a commercial source of hypochlorous acid. It is only moderately soluble in water.

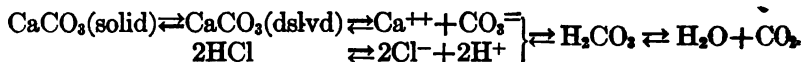
**Hypochlorous Acid from Bleaching Powder.**—1. When bleaching powder is dissolved in water, being a salt, it is very extensively ionized (see formulation, below). If now an *active* acid, that is, one giving a large concentration of hydrogen-ion, is added, the values of the products of the concentrations  $(\text{H}^+) \times (\text{Cl}^-)$  and  $(\text{H}^+) \times (\text{OCl}^-)$ , on which depend the extent to which molecules of  $\text{HCl}$  and  $\text{HOCl}$  will be formed (p. 359), are large.  $\text{HClO}$ , being little ionized, is formed extensively:  $\text{HCl}$ , being highly ionized is formed in much smaller amount. Both, however, interact to produce chlorine and water, and this displaces the other equilibria. Hence an active acid decomposes the salt almost completely. An active acid gives, therefore, chlorine-water, and not pure hypochlorous acid.





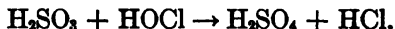
When the dilute mixture is distilled, chlorine monoxide ( $2\text{HOCl} \rightleftharpoons \text{H}_2\text{O} + \text{Cl}_2\text{O}$ ) passes over with the steam, and so a dilute hypochlorous acid can be obtained.

**Hypochlorous Acid from Chlorine-Water.** — An interesting way of obtaining dilute hypochlorous acid is to add chalk  $\text{CaCO}_3$  to chlorine-water and distil. Here, the chalk is *insoluble*, and so gives a very low concentration of  $\text{Ca}^{++} + \text{CO}_3^{=}$ . The  $\text{HCl}$  in the chlorine-water gives, however, a sufficiently large concentration of  $\text{H}^+$  to combine with the  $\text{CO}_3^{=}$  to form  $\text{H}_2\text{CO}_3$ , which is hardly ionized at all. This carbonic acid  $\text{H}_2\text{CO}_3$  then decomposes and carbon dioxide is liberated:

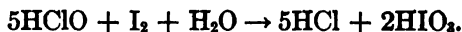


The hypochlorous acid, however, remains molecular  $\text{HOCl}$ , gives almost no  $\text{H}^+$ , and so for the most part remains unaffected. It can afterwards be distilled off with the water.

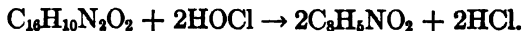
**Hypochlorous Acid as an Oxidizing Agent.** — Hypochlorous acid, in decomposing into oxygen and hydrochloric acid, gives off heat.  $\text{HOCl, Aq} \rightarrow \text{HCl, Aq} + \text{O} + 9300 \text{ cal.}$  Hence more energy is liberated in oxidation by the acid than in oxidation by free oxygen, and the acid is therefore more active as an oxidizing agent (p. 314). Thus, hypochlorous acid, either in pure solution or in the form of chlorine-water, oxidizes sulphurous acid instantly:



It also oxidizes bromine and iodine, in water, although these elements are not affected by free oxygen, giving bromic and iodic acids, respectively:



The solution also oxidizes organic colored substances (p. 315), producing colorless, or less strongly colored ones. Thus, it oxidizes indigo (deep blue) quickly to isatin, a yellow substance relatively pale in color:



In ways just as definite as this, hypochlorous acid will change the composition of other colored substances, although, since we do not know the formulæ of all these substances, we cannot always write equations for the actions. Thus, the interaction by which chlorophyll, the green coloring matter of plants, is bleached is doubtless similar to the above, although the formulæ of materials concerned are unknown.

**Hypochlorous Acid as a Bleaching Agent.** — It is on account of its oxidizing power that hypochlorous acid is used commercially in bleaching. It is not applied to paints, which are chiefly mineral substances, but to complex compounds of carbon, such as constitute the coloring matters of plants and of those artificial dyes which are now manufactured in great variety. It should be understood that the great majority of the complex compounds of carbon are colorless. Even a slight chemical change, affecting only one or two of the atoms in a complex molecule, is thus almost sure to give a colorless or much less strongly colored material.

Cotton and linen, in their original states, are not pure white. Bleaching is, therefore, an extensive and most important industry. The yarn or cloth must first be freed from cotton-wax and tannin, since the former would protect it from the action of the bleaching agent, and both would make the subsequent dyeing uneven. The material is, therefore, first boiled with very dilute sodium hydroxide solution, and washed with water. The goods are then saturated with bleaching powder solution, and piled loosely until the coloring matter has been oxidized. They are finally washed with extreme thoroughness.

As a rule, an active acid is not added. The bleaching is produced by the hypochlorous acid liberated by the action of the carbon dioxide from the air. The carbon dioxide dissolves in the water of the solution on the goods, and forms carbonic acid:  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$  (see p. 476, par. 1). The subsequent washing removes all traces of the bleaching powder, of the lime which the powder often contains, and of the hypochlorous acid, which otherwise would act gradually upon the cotton or linen and "rot" it. Bleaching agents, when used in the household without sufficiently careful, subsequent washing, are liable to cause serious damage from this cause.

Cotton and linen are composed of cellulose  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , a rather inert substance, and one which is very slowly acted upon by dilute

hypochlorous acid. Hence, with brief contact and proper handling, no damage is done. Wool, silk, and feathers, however, are composed largely of compounds (proteins) containing nitrogen (up to 15 per cent), in addition to the above three elements. Their constituent material interacts as easily with hypochlorous acid as do the traces of coloring substances. Hence, since the fabric itself would be attacked by this agent, sulphur dioxide or sulphurous acid (p. 445) is used for bleaching these materials.

It should be understood that a cold dilute solution of hypochlorous acid may be kept (in the dark) almost indefinitely and will not give up its oxygen spontaneously. The transfer takes place when, and only when, the acid comes in contact with some substance capable of uniting with oxygen.

***Bleaching Powder in Sanitation.*** — A disinfectant is a substance which destroys bacteria and other minute organisms. Bleaching powder has a distinct odor of chlorine monoxide (*not* chlorine). This is due to the action of atmospheric carbon dioxide liberating hypochlorous acid (p. 476). The dry powder therefore will disinfect the air and surrounding objects. It must be used with discretion, however, as the gas is very corrosive.

As already mentioned (p. 142), in the purification of city waters the organisms (associated in some way with colon bacilli) which give rise to typhoid fever are destroyed by adding a small proportion of bleaching powder in the form of a 2 per cent solution (about 17–24 lbs. of the powder per million gallons of water). The salt is hydrolyzed (p. 398), giving a basic calcium chloride and free hypochlorous acid. The latter kills the organisms, and is itself decomposed in the process, so that nothing offensive remains in the water. There is only a minute increase in the proportion of salts of calcium (hardness). Sewage is sometimes freed from pathogenic organisms in the same way.

Recently, chlorine-water, made by use of cylinders of liquid chlorine (p. 221), has in many cases taken the place of bleaching powder solution for this purpose.

***Chlorine not a Bleaching Agent.*** — Chlorine itself is often, erroneously, described as a bleaching agent. If a dry, colored cloth be hung for a week in chlorine gas, dried by a little sulphuric acid in the bottom of the bottle (Fig. 114), little or no change in the color will occur. But a *wet* rag is bleached as soon as the chlorine

has time to dissolve in the water and give the necessary hypochlorous acid. Flowers are bleached by dry chlorine gas, because by their nature they contain the indispensable water.

**Thermochemistry of Hypochlorous Acid.** — As we have seen (p. 35), chemical changes which proceed spontaneously are accompanied by a transformation of free internal energy into some other form of energy. Hence, a substance, or system of substances, which undergoes such a change, possesses more chemical energy and activity before the change than after it. In consequence, if some given chemical change *uses* the products of such an action, and can be brought about by the employment of the original substance, the employment of the latter will involve a greater liberation of energy, and will therefore be more likely to secure the consummation of the change in question.

The decomposition of hypochlorous acid and of chlorine monoxide are cases where there is a very marked difference between the amount of chemical energy in the original substances and in the products of decomposition, hydrogen chloride and free oxygen in the first case, and free chlorine and oxygen in the second. Hence the changes into these substances sometimes are of the nature described as explosive. A more important fact, however, is that, on this account, hypochlorous acid and chlorine monoxide are more active oxidizing agents than is free oxygen gas. The energy liberated in the decomposition of the hypochlorous acid has to be *added* (p. 315) to that which free oxygen could give, if performing the same oxidation, in order that the *total fall in energy*, which measures the tendency of the action to take place, may be estimated. Hence, substances that are not affected by free oxygen may be changed instantly by hypochlorous acid. This explains, for example, the oxidation by hypochlorous acid of many carbon compounds, including those which are colored, when atmospheric air is without action. Thus, the heat liberated in the oxidation of indigo to isatin by oxygen gas, if it could be carried out, would be 1800 cal. The much greater heat liberated when hypochlorous acid is used, we obtain by adding the thermochemical equations:

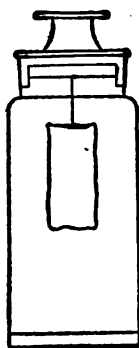
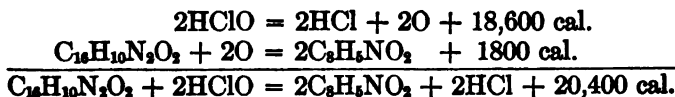


FIG. 114.

The following thermochemical equations give a rough idea of the relative oxidizing powers of the chief oxygen acids of the halogens:

$\text{HClO}, \text{Aq} = \text{HCl}, \text{Aq} + \text{O} + 9,300 \text{ cal.}, \text{ or } + 9,300$	} cal. for each atomic weight of oxygen.
$\text{HClO}_2, \text{Aq} = \text{HCl}, \text{Aq} + 3\text{O} + 15,300 \text{ cal.}, \text{ or } + 5,100$	
$\text{HClO}_3, \text{Aq} = \text{HCl}, \text{Aq} + 4\text{O} + 700 \text{ cal.}, \text{ or } + 170$	
$\text{HBrO}_2, \text{Aq} = \text{HBr}, \text{Aq} + 3\text{O} + 15,000 \text{ cal.}, \text{ or } + 5,000$	
$\text{HIO}_3, \text{Aq} = \text{HI}, \text{Aq} + 3\text{O} - 42,900 \text{ cal.}, \text{ or } - 14,300$	
$\text{HIO}_4, \text{Aq} = \text{HI}, \text{Aq} + 4\text{O} - 34,500 \text{ cal.}, \text{ or } - 8,600$	

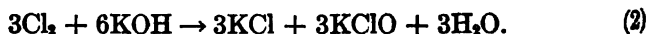
Formerly a different explanation for actions like that of hypochlorous acid, when it behaves as an oxidizing agent, was offered. It was suggested that the oxygen was first liberated from the acid:  $\text{HOCl} \rightarrow \text{HCl} + \text{O}$ , and that the single atoms of the element so produced were more active than molecular oxygen. Exactly how the hypochlorous acid, lacking all consciousness, knew that an oxidisable body was present, and proceeded to liberate the atoms of oxygen, was never explained. This oxygen, which was supposed to interact in the moment of its production, was called **nascent oxygen**. But it will be seen that such an explanation is entirely unnecessary. The activity of the hypochlorous acid on account of its large store of free energy sufficiently accounts for the facts (see Nascent hydrogen).

**Chemical Properties of Hypochlorites.**—When hypochlorites are heated they change into chlorates (see below). They may also give off oxygen,  $2\text{CaCl}(\text{OCl}) \rightarrow 2\text{CaCl}_2 + \text{O}_2$ . Although this decomposition is slow in cold solutions of hypochlorites, or when they are preserved in the dry form, it may be hastened by means of catalytic agents. The addition of a little cobalt hydroxide (*q.v.*) to a paste of bleaching powder and water causes rapid evolution of oxygen.

**Chlorates.**—Like hypochlorous acid itself, the hypochlorites turn into chlorates. Thus, when chlorine is passed into a warm, concentrated solution of potassium hydroxide, and particularly when an excess of chlorine is used, the potassium hypochlorite changes into **potassium chlorate**  $\text{KClO}_3$  as fast as it is formed:



To secure the three molecules of the hypochlorite, the equation formerly given (p. 475) must be tripled:



When these are added, and the intermediate substance is left out, the final equation is obtained:

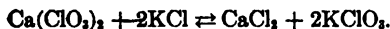


When the solution is cooled, the less soluble chlorate crystallizes out.

This action involves converting five-sixths of the valuable potassium hydroxide into the relatively less valuable potassium chloride. Hence, in practice, the makers carry out the corresponding action with calcium hydroxide. They then add potassium chloride to the resulting solution, containing calcium chloride and calcium chlorate  $\text{Ca}(\text{ClO}_3)_2$  (sol'ty 175 : 100 Aq,  $18^\circ$ ). The potassium chlorate (sol'ty 6.6 : 100 Aq,  $18^\circ$ ), formed by double decomposition, crystallizes when the solution is cooled.

All chlorates are at least moderately soluble in water (see Table inside front cover). Potassium chlorate is used in making fireworks, explosives, and matches. An intimate mixture with sugar  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  burns with semi-explosive violence, the oxygen of the salt combining with the carbon and hydrogen to form carbon dioxide and water.

**The Separation of Substances by their Solubility.**—When neither of the products of an action approaches absolute insolubility, a separation may nevertheless be effected more or less perfectly by taking advantage of difference in solubility. Thus, in the practical method of making potassium chlorate, the calcium chloride is exceedingly soluble, while the potassium chlorate is only moderately so. Then, too, the solubility of the latter decreases rapidly as the temperature is lowered (Fig. 79, p. 191). Hence, it is found that when the mixture is cooled to  $-18^\circ$  only about 13.5 g. of potassium chlorate remain dissolved in each liter, and are lost. At  $0^\circ$  the loss would be greater, for at this temperature a liter of pure water would hold 33.3 g., and a liter of this solution would contain more than this on account of the uncompleted reversible action (cf. p. 381):



It will be seen that we reason as if the solubility of each substance was independent of the presence of other dissolved bodies (p. 187).

By the use of this principle, and the data in regard to solubility in Fig. 79 (p. 191), a rough idea may be obtained of what may be expected in any given case. From the diagram the solubilities at any given temperature may be read. Suppose, for example, the question is in regard to the quantity of potassium chlorate we may expect to obtain from 3 g. of potassium hydroxide dissolved in 7 g. of water (a 30 per cent solution). From the equation:



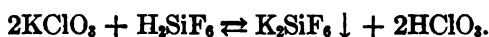


we find that 336 g. of potassium hydroxide give 122.5 g. of chlorate and 372.5 g. of chloride. Hence, by proportion, 3 g. will give about 1 g. and 3 g. respectively. The solubility, read from the diagram, is the amount of the salt dissolved by 100 c.c. of water, for example, 56.5 g. of potassium chloride at 100°. Some of the results are given in the form of a table:

	POTASSIUM CHLORIDE.	POTASSIUM CHLORATE.
Amount formed from 3 g. KOH . . . . .	3.0	1.0
Solubility at } 100 c.c. Aq. . . . .	56.5	56.5
100° in } 7 c.c. Aq. . . . .	4.0	4.0
Solubility at } 100 c.c. Aq. . . . .	34.7	7.5
20° in } 7 c.c. Aq. . . . .	2.5	0.5
Solubility at } 100 c.c. Aq. . . . .	28.0	3.3
0° in } 7 c.c. Aq. . . . .	2.0	0.25

Thus, at 20°, at least 2.5 g. of the 3 g. of potassium chloride will remain dissolved, while half of the potassium chlorate will crystallize out. If the solubilities are examined, it will be seen that the potassium chlorate is even more easily obtainable in pure condition when calcium chloride takes the place of potassium chloride.

**Chloric Acid.**— Since none of the acids of this series can be obtained by direct union of their elements (p. 472), it is usual first to prepare the salts, and to make the acids from the salts by double decomposition. This acid may be obtained in solution in water, by adding the calculated amount of hydrofluosilicic acid to a solution of potassium chlorate:



The potassium fluosilicate, being insoluble, is removed by filtration. It will be noted that double decomposition, involving precipitation, may thus be used for obtaining a soluble product, as well as an insoluble one (cf. selenic acid, p. 454).

The statement commonly made that chloric acid is prepared by adding dilute sulphuric acid to barium chlorate solution:  $\text{Ba}(\text{ClO}_3)_2 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{BaSO}_4 \downarrow + 2\text{HClO}_3$ , is interesting. Barium chlorate is itself made from chloric acid and barium hydroxide! The action of chlorine upon a solution of the latter substance cannot be used, because the chlorate and chloride of barium are equally soluble (see Table), and cannot be separated by partial crystallization.

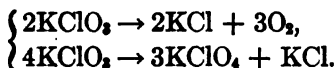
The solution of chloric acid may be concentrated (to about 40 per cent) by evaporation, but must not be heated above 40°, as the

acid decomposes near this temperature. The resulting thick, colorless liquid has powerful oxidizing qualities, setting fire to paper (made of cellulose  $C_6H_{10}O_5$ ) which has been dipped into it. It converts iodine into iodic acid,  $5HClO_3 + 3I_2 + 3H_2O \rightarrow 6HIO_3 + 5HCl$ . When warmed beyond  $40^\circ$  the acid decomposes, giving chlorine dioxide and perchloric acid:



**Chlorine Dioxide: Chlorous Acid.**—Chlorine dioxide  $ClO_2$  (see above) is a yellow gas which may be liquefied, and boils at  $+10^\circ$ . The gas and liquid are violently explosive, the substance being resolved into its elements with liberation of much heat. It is formed whenever chloric acid is set free, and hence it is seen when a little powdered potassium chlorate is touched with a drop of concentrated sulphuric acid (end of last section).<sup>\*</sup> Concentrated hydrochloric acid turns yellow from the same cause when any chlorate is added to it. These actions are used as tests for chlorates, and distinguish them from perchlorates (*q.v.*). With water, chlorine dioxide gives a mixture of chlorous acid  $HClO_2$  and chloric acid, and with bases a mixture of the chlorite and chlorate.

**Perchlorates.**—When heated, chloric acid and chlorates give perchloric acid (p. 483) and perchlorates respectively. The chlorates also give oxygen at the same time (p. 83):

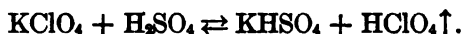


These actions, like the three decompositions of hypochlorous acid (p. 474), are independent, and proceed simultaneously. They are concurrent reactions (p. 485). Their relative speed, however, varies with the temperature, and the decomposition into chloride and oxygen may completely outrun the other when a catalytic agent like manganese dioxide, which hastens only one of the two actions, is added (p. 97). When pure potassium chlorate is heated cautiously, about one-fifth of it has lost all its oxygen by the time the rest has turned into perchlorate. The mixture may be separated

<sup>\*</sup> The mixture of sugar and potassium chlorate (p. 481) can be set on fire by a drop of sulphuric acid [Lect. exp.]. The latter liberates chloric acid, which in turn gives  $ClO_2$ , and the latter, being a violent oxidizing agent, starts the combustion of the sugar.

by grinding with the minimum quantity of water which will dissolve the chloride it contains. The perchlorate, having at  $15^{\circ}$  less than one-twentieth of the solubility of the chloride, will remain, for the most part, undissolved. The perchlorates are much more stable (p. 148) than the chlorates, or hypochlorites: they are all soluble in water, and they are used in making matches and fireworks.

**Perchloric Acid  $\text{HClO}_4$  and Perchloric Anhydride  $\text{Cl}_2\text{O}_7$ .—** Pure perchloric acid explodes when heated above  $92^{\circ}$ . But, like other liquids, its boiling-point is lower when its vapor is under reduced pressure (cf. p. 146). At 56 mm. pressure it boils at  $39^{\circ}$ , a temperature at which hardly any decomposition is noticeable. Hence the acid may be made by mixing potassium perchlorate and concentrated sulphuric acid and distilling the mixture cautiously in a vacuum (p. 316).



Perchloric acid is a colorless liquid, which decomposes, and often explodes spontaneously, when kept. A 70 per cent solution in water is perfectly stable, however. Although it is an active oxidizing agent, it is not so active as chloric acid, and does not oxidize hydrogen chloride in cold aqueous solution. Hence a drop of hydrochloric acid placed on a crystal of a perchlorate gives no yellow color. When the acid is liberated by concentrated sulphuric acid, it does not at once give the yellow chlorine dioxide (p. 483).

**Perchloric anhydride  $\text{Cl}_2\text{O}_7$**  may be prepared by adding phosphoric anhydride to perchloric acid in a vessel immersed in a freezing mixture,  $\text{P}_2\text{O}_5 + 2\text{HClO}_4 \rightarrow 2\text{HPO}_3 + \text{Cl}_2\text{O}_7$ . Phosphoric anhydride is often used in this way for removing the elements of water from compounds. It combines with water to form metaphosphoric acid  $\text{HPO}_3$ . By gently warming the mixture, the perchloric anhydride can be distilled off. It is a colorless liquid boiling at  $82^{\circ}$  (760 mm.), and exploding when struck or too strongly heated.

**Relation of Anhydride and Acid or Salt.**—The derivation of the formula of the anhydride from [that of the acid or salt should receive special attention. In the mind of the chemist, the one always instantly suggests the other, so often does he think of them as potentially the same substance. The beginner, however, finds this habit hard to acquire, and indeed is more likely to blunder, in trying to divide the formula of an acid into the formulae of water and the anhydride, than in any other calculation he makes.

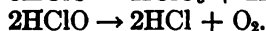
The rule is: If the formula of the acid shows an *even* number of hydrogen atoms ( $\text{H}_2\text{SO}_4$  or  $\text{H}_4\text{SiO}_4$ ), subtract all the elements of water ( $\text{H}_2\text{O}$  or  $2\text{H}_2\text{O}$ ), and the balance is the anhydride ( $\text{SO}_2$  or  $\text{SiO}_2$ ). The divided formulæ are  $\text{H}_2\text{O}, \text{SO}_2$  or  $2\text{H}_2\text{O}, \text{SiO}_2$ . If there is an *odd* number of hydrogen atoms ( $\text{HClO}_4$  or  $\text{H}_3\text{PO}_4$ ) double the formula ( $\text{H}_2\text{Cl}_2\text{O}_8$  or  $\text{H}_6\text{P}_2\text{O}_8$ ), and subtract all the elements of water as before ( $\text{Cl}_2\text{O}_7$  or  $\text{P}_2\text{O}_5$ ). Then check the result, by adding the water again, and dividing by two, correcting the blunder if one has been made.

If the substance is a salt ( $\text{CuSO}_4$  or  $\text{KClO}_4$ ), subtract the oxide of the metal ( $\text{CuO}$  or  $\text{K}_2\text{O}$ ), taking care to assign to the metal the same valence in the oxide as it shows in the salt ( $\text{SO}_3$  or  $\text{Cl}_2\text{O}_7$ ).

There are several uses for this art of ascertaining the anhydride corresponding to a given salt or acid. One is in the making of equations (*e.g.*, pp. 496, 535). Another is in finding the valence of the non-metal. Thus, in  $\text{KClO}_4$  the anhydride is  $\text{Cl}_2\text{O}_7$ , and the valence of the chlorine is seven. In  $\text{H}_3\text{PO}_4$  the anhydride is  $\text{P}_2\text{O}_5$ , and the phosphorus quinquivalent. In  $\text{HPO}_3$  (metaphosphoric acid), the anhydride is again  $\text{P}_2\text{O}_5$ , and the phosphorus is therefore in the same state of oxidation — both are phosphoric acids.

### *Simultaneous Chemical Changes in the Same Substances.*

— When two or more reactions go on simultaneously in the same materials, the actions may be consecutive (p. 445) or they may be parallel. In the latter case they are called **concurrent reactions**. Thus, hypochlorous acid undergoes three different changes:



Some molecules decompose into water and chlorine monoxide (p. 474), while others give chloric acid and hydrogen chloride, and still others hydrogen chloride and oxygen. Since the *same molecule* cannot undergo more than one of these different changes, it follows that the actions are *independent* of one another. This is shown by the fact that in sunlight the third predominates, while in the dark it falls far behind the second. Since the *relative* quantities of the products vary, the **several simultaneous actions cannot be put in the same equation**. The fundamental property of an equation is to show the *constant* proportions by weight between every pair of substances in it. Hence three separate equations are required in

the present, and in all similar cases where all the proportions are not constant. Thus, again, in the decomposition of potassium chlorate by heating (p. 483), it would be misleading and wrong to add the two equations together and write, for the whole action:



This equation would mean that the proportions amongst the products were always  $\text{KCl} : \text{KClO}_4 : \text{O}_2$  or 74.6 : 138.6 : 32, whereas, in fact, the proportions vary with the conditions—the temperature used or the presence of a catalyst which hastens one action but not the other.

**Consecutive reactions** (p. 445), however, like (1) followed by (2) on pp. 433, 474, may be combined in one equation, since in them all the proportions must necessarily be constant. These equations are interlocked, for (2) consumes what (1) produces.

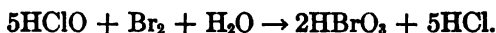
**Oxygen Acids of Bromine.**—No oxides of bromine have been made, but the acids  $\text{HBrO}$  (hypobromous acid) and  $\text{HBrO}_3$  (bromic acid) and their salts are familiar.

By the action of bromine on dilute, cold potassium hydroxide solution, the **bromide** and **hypobromite** are formed:



When the solution is heated, the hypobromite turns into **potassium bromate**  $\text{KBrO}_3$  and bromide. The actions are exact parallels of the corresponding ones for chlorine (pp. 474, 480).

Aqueous bromic acid  $\text{HBrO}_3$  may be made in the same way as chloric acid (p. 482), or by the action of chlorine-water on bromine:



The solution is colorless and has powerful oxidizing properties. Thus, it converts iodine into iodic acid:  $2\text{HBrO}_3 + \text{I}_2 \rightarrow 2\text{HIO}_3 + \text{Br}_2$ . It appears, therefore, that iodine has more affinity for oxygen than has bromine.

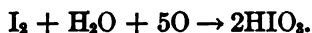
**Oxide and Oxygen Acids of Iodine.**—The following are the acids and their corresponding salts:

[HIO	Hypoiodous acid],	[KIO	Potassium hypoiodite],
HIO <sub>3</sub>	Iodic acid,	KIO <sub>3</sub>	Potassium iodate,
[HIO <sub>4</sub>	Periodic acid],	NaIO <sub>4</sub>	Sodium periodate,
H <sub>5</sub> IO <sub>6</sub>	Periodic acid,	Na <sub>2</sub> H <sub>3</sub> IO <sub>6</sub>	Disodium periodate.

The substances in parenthesis have not been isolated. There is one oxide, iodic anhydride  $I_2O_5$ .

**Iodates and Iodic Acid.**—The potassium and sodium salts of iodic acid are found in Chile saltpeter. They may be made, in much the same fashion as are the chlorates and bromates (p. 481), by adding powdered iodine to a hot solution of potassium or sodium hydroxide. There is evidence that hypoiodites are formed in cold solutions, but they change quickly to iodates. It is disodium periodate  $Na_2H_3IO_6$ , however, which, being the least soluble, crystallizes out.

**Iodic acid**  $HIO_3$  is formed by passing chlorine through powdered iodine suspended in water. The action is parallel to that of chlorine on bromine water. A still better way is to boil iodine with aqueous nitric acid (*q.v.*). The latter gives up oxygen readily, and is here used solely on this account. Hence it may be omitted from the equation, only the oxygen, of which it is the source, appearing:



In both these actions the initial substances (including the excess of nitric acid) and the products, with the exception of the iodic acid itself, are all volatile. When the solution is concentrated by evaporation, the iodic acid crystallizes. It is a white solid, perfectly stable at ordinary temperatures, and can be kept indefinitely. At  $170^\circ$  it begins to give off water vapor  $2HIO_3 \rightleftharpoons H_2O + I_2O_5$ , leaving **iodic anhydride**. The latter is a white crystalline powder which may be raised to  $300^\circ$  before it, in turn, breaks up, giving iodine and oxygen.

In aqueous solution iodic acid is an oxidizing agent, but does not part with its oxygen so readily as do chloric acid and bromic acid. It oxidizes hydrogen iodide in dilute solution:  $HIO_3 + 5HI \rightarrow 3H_2O + 3I_2$ , all the iodine being liberated. In this respect it resembles concentrated sulphuric acid (p. 438). Dilute sulphuric acid shows no oxidizing qualities.

**Various Acids Derived from One Anhydride.**—Some acids are related to their anhydrides as are hypochlorous acid (p. 473) and sulphurous acid (p. 444). One molecule of the anhydride combines with one molecule of water. In other cases, however, the proportion of water may be less or greater than this. Now if periodic acid were of the former type ( $H_2O, I_2O_7 = 2HIO_4$ ), its formula would be  $HIO_4$ . It does form *salts* of this type, such as  $NaIO_4$  and  $AgIO_4$ .

But the free acid is a deliquescent solid of the formula  $\text{H}_5\text{IO}_6$  ( $= 5\text{H}_2\text{O} \cdot \text{I}_2\text{O}_7$ ), and the most easily prepared salt belongs to this type. *All types are called periodates, however, because their compositions are all founded upon the same anhydride.* The latter has not itself been made. We usually speak of various acids and salts as being **derived from** the same anhydride, the word "derived" being used in a figurative and not a literal sense.

The difference between two acids  $\text{HIO}_4$  and  $\text{H}_5\text{IO}_6$  is not at all the same as between  $\text{HIO}_3$  and  $\text{HIO}_4$ . The latter would represent different stages of oxidation, being derived from  $\text{I}_2\text{O}_5$  and  $\text{I}_2\text{O}_7$ , respectively, and accordingly would be named iodic acid and periodic acid. The former differ only by  $2\text{H}_2\text{O}$ , and an addition or subtraction of the elements of water *in equivalent quantities* is neither oxidation nor reduction. Hence they are both periodic acids (see Phosphoric acid).

**Periodates and Periodic Acid.**—Sodium periodate  $\text{NaIO}_4$  is found in Chile saltpeter. When sodium iodate  $\text{NaIO}_3$  is dissolved along with sodium hydroxide in water, and chlorine is passed into the mixture, the sodium hypochlorite formed from the latter oxidizes the iodate  $\text{NaIO}_3 + \text{O} \rightarrow \text{NaIO}_4$ . But the somewhat insoluble salt which crystallizes out is  $\text{Na}_2\text{H}_3\text{IO}_6$ :



Other salts may be made from this one.

An aqueous solution of periodic acid is obtained by the action of sulphuric acid on barium periodate, followed by filtration. A white, very soluble solid  $\text{H}_5\text{IO}_6$  remains when the liquid is evaporated. When this is heated, water and oxygen are both given off, and iodine pentoxide  $\text{I}_2\text{O}_5$  alone remains.

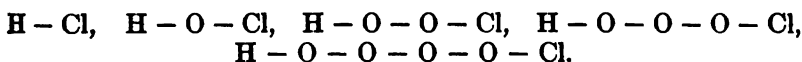
**Chemical Relations.**—The compounds of the halogens with metals and with hydrogen diminish in stability, with ascending atomic weight of the halogen, in the order: F (19), Cl (35.5), Br (80), I (127). Each halogen will displace those following it from *this kind of combination*. In the case of the oxygen compounds, the order of stability is just the reverse, those of iodine, for example, being the only ones which are reasonably stable.

Amongst the oxygen acids of any one halogen, those containing most oxygen are most stable. The salts are in all cases more stable by far than the corresponding acids.

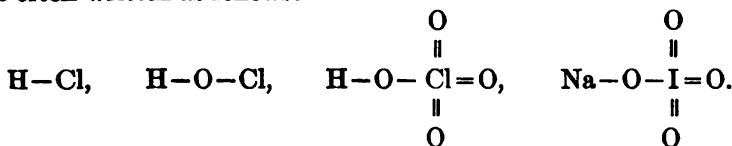
The halogens when combined with metals or hydrogen are univa-

lent (HI, KCl, etc.). It is clear, however, that, when united with oxygen, their valence is higher. The maximum is shown in perchloric anhydride  $\text{Cl}_2\text{O}_7$ , where chlorine is septivalent.

The formulæ of the acids might be written so as to retain the univalence:



But compounds in which we are *compelled* to believe that two oxygen units are united are usually unstable (*e.g.*, hydrogen peroxide,  $\text{H} - \text{O} - \text{O} - \text{H}$ ), and we should expect the instability would be greater with three and with four units of oxygen in combination. Here, however, the reverse state of affairs must be taken account of in our formulæ, for  $\text{HClO}_4$  is the most stable of the chlorine set. This reasoning, together with the septivalence in  $\text{Cl}_2\text{O}_7$ , leads us to assume the valence seven in perchloric acid (see Periodic system). The structural formulæ (*cf.* p. 442) of some of these substances are therefore often written as follows:



**The Specification of Chemical Properties.** — The chemical properties of a substance are frequently specified so loosely that the student has no definite guide before him. The following illustrates the scheme that should be kept in mind.

1. **Stability** (p. 148), particularly if a compound, but applicable also to elements like iodine (p. 276). Mention products of decomposition.

2. **Molecular weight**, if known.

3. **Class to which the substance belongs**, and indication of degree of activity where possible, such as simple substance, weak acid, active base, salt, carbohydrate, etc. Terms like acid, base, and salt imply certain properties, which need not be given in detail.

4. **Substances with which combination occurs**, such as the metals (exceptions named), the non-metals (exceptions named), water, ammonia, etc. The class to which the resulting compounds belong should be named.

5. **Oxidising or reducing agent**, if such, with illustrations and indication of limitations.

6. **Other specific chemical reactions**, such as hydrolysis, if a salt; action of chlorine, if a hydrocarbon; etc.

**Each chemical property should specify directly** (or by implication, *e.g.*,



by using the word base) **some definite variety of chemical change, or kind of chemical behavior**, and should name the materials or classes of materials involved.

The **chemical relations** are not properties of a *substance*, but qualities of an element in combination, such as atomic weight, valence, non-metallic or metallic element (oxide acidic or basic, halides hydrolyzed or not). They have been discussed elsewhere (pp. 226, 464).

It may be well to illustrate inept ways of giving chemical properties. "Oxygen supports combustion of a candle." The beginner does not know that a candle is composed of a cotton wick surrounded by a mixture of hydrocarbons and fatty acids, so no chemical reaction can be extracted by him from this statement. The chemical property is the tendency of compounds of carbon and hydrogen to interact vigorously with oxygen, giving water and carbon dioxide. The burning of a candle for light is an *application* of this property, *but is not the property itself*. Applications should be given, of course, but they should follow the property, not displace it. Similarly, "bleaching ability" is often given as a chemical property. But sodium hyposulphite and other substances bleach indigo by reducing it to indigo white, and hypochlorous acid and ozone bleach indigo by oxidizing it to isatin, sodium hydroxide bleaches blue prints because it is an active base and interacts with the ferrous ferricyanide, and water and other solvents sometimes bleach by dissolving the dye. Bleaching may, therefore, be due to entirely different chemical or physical properties in different cases. It is an *application* of some specific chemical property, and should be given as an illustration of the use of the property. Similarly, "disinfecting power" in the case of hypochlorous acid or hydrogen peroxide is due to oxidation of the unstable substances in the pathogenic organisms, but sulphurous acid adds itself to the aldehydes which their protoplasm contains, alcohol (used, *e.g.*, to sterilize the skin before vaccination) takes the place of the moisture in the organisms, killing them by physical means, and formaldehyde is a reducing agent, and is also able to add itself to, or to give condensations with, many organic compounds. Disinfecting power is thus an *application* of one of the foregoing, or of some other property, which should first be specified. When a substance is poisonous, this should be emphasized, but not given as a chemical property. Even when the chemical changes, which the poisons bring about in the body, are known, they can seldom be explained in inorganic or elementary general chemistry.

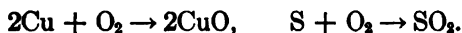
Again the phrase "supports combustion" is of uncertain meaning. In ordinary language it refers to fuels like wood and coal. To say that "chlorine supports combustion," is therefore, not specific enough. Coal and wood will not burn in it. Iron, copper, and antimony will, but if these substances are not named, the statement leaves the reader to supply the very information which he lacks, and which the book should have furnished. Still again, the statement that chlorine combines with copper and sodium omits to make it clear that chlorine combines easily with all the familiar metals, excepting platinum and gold. If each individual element with which chlorine combines is to constitute a separate chemical property, then, with only two elements named, the list of this class of properties

is very incomplete, since it includes only two out of about sixty-five. Naming the *class* of elements, with illustrations and exceptions, covers the point, and puts less strain upon the memory.

Negative statements convey little information. "Nitrogen will not support combustion." This means, either that coal and tapers will not burn in it, in which case it should be explained that carbon and hydrogen do not readily unite with nitrogen, or else that nitrogen is not oxygen! Chemical properties should be stated positively, not reached indirectly, by excluding one by one all the things the substance cannot do. Nitrogen does not bleach, does not burn, and can neither climb a tree nor eat grass — but a hundred negative items will still leave us ignorant of what it *can* do. When two elements are very similar, yet one has a property which the other lacks, it is instructive, and therefore desirable, to mention the absence of the property, but such cases are rare. To parade as a property of phosphorus pentoxide that it is not combustible, is like saying that a bankrupt cannot pay his debts — it is redundant. Even more absurd is the statement, when given as a property, that chlorine is formed by oxidation of hydrochloric acid. This is a property of the acid and oxidizing agent. Chlorine has no properties as a substance until after it has been formed.

## OXIDATION AND REDUCTION

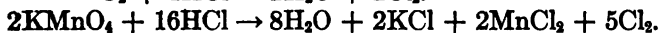
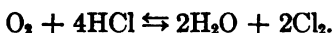
**Oxidation by Oxygen.** — The simplest oxidations are the cases where a metal or non-metal *unites with oxygen*:



Union of a compound with *additional oxygen* is oxidation also.



The *removal of hydrogen* from hydrogen chloride (preparation of chlorine, p. 217), is also defined as oxidation.



*Every oxidation is accompanied by reduction of the oxidizing agent.* Thus, in the second last equation, the free oxygen is reduced to water. Again, in the third last equation,  $2\text{KClO}$  is reduced to  $2\text{KCl}$ , while  $1\text{KClO}$  becomes  $\text{KClO}_3$  by oxidation.

In the laboratory, we frequently discover that an oxidation has occurred by noticing the presence of a product of reduction. Thus, when we heat carbon with sulphuric acid:  $2\text{H}_2\text{SO}_4 + \text{C} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 2\text{SO}_2$ , we do not notice the product of oxidation,  $\text{CO}_2$ , because it is odorless and colorless, but we perceive at once the *odor* of the sulphur dioxide, and realize that the sulphuric acid

must have oxidized some substance, for this gas could not have been formed (at the temperature employed) except by reduction.

Note that the removal of the elements of water is *neither oxidation nor reduction*, for equivalent amounts of both oxygen and hydrogen are removed:



*In all the cases discussed above, oxidation consists in adding oxygen or removing hydrogen.*

**Oxidation by Other Negative Elements.**—Oxygen is only one of the class of elements called non-metallic or negative elements, so we cannot logically *restrict* the term “oxidation” to actions involving oxygen. Thus, forming a chloride, or increasing the proportion of chlorine in a compound is oxidation:



In every compound, one of the elements is relatively positive and the other relatively negative. Thus, copper is positive and chlorine negative. In carbon dioxide  $\text{CO}_2$ , carbon is (relatively) positive and oxygen negative, and in calcium carbide  $\text{CaC}_2$  calcium is positive and carbon (relatively) negative.

Thus, **oxidation is introducing, or increasing the proportion of the negative element, or removing, or reducing the proportion of the positive element.** Reduction is the converse.

**Oxidation and Valence.**—Combining a metal with oxygen or sulphur raises the *active valence* of the metal from zero to some finite value:  $2\text{Cu}^0 + \text{O}_2^0 \rightarrow 2\text{Cu}^{\text{II}}\text{O}^{\text{II}}$ . *Metallic* copper has *no valence in use*. In  $\text{CuO}$  or  $\text{CuCl}_2$  it has gained the valence II. The copper has been oxidized. Similarly, changing  $\text{FeCl}_2$  into  $\text{FeCl}_3$  increases the active valence of the iron from II to III (oxidation). Conversely, changing  $2\text{HCl}$  to  $\text{Cl}_2$  decreases the active valence of chlorine from I to zero (oxidation). In the same equation (p. 218),  $\text{KMn}$  in  $\text{KMnO}_4$  must have a total valence of VIII, but in the products  $\text{KCl} + \text{MnCl}_2$  the total valence has decreased to III (reduction).

Again, in displacement, *e.g.*,  $\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2$ , the zinc is oxidized because the active valence goes from zero to II, and the hydrogen is reduced.

Hence, **oxidation consists in increasing the active valence of a**

positive element or decreasing that of a negative element. Reduction is the converse.

This way of stating the rule makes it clear why removing the elements of water is neither oxidation nor reduction. We are removing *both* a positive and a negative element, and are removing them in *equi-valent* amounts,  $2\text{H}^+ + \text{O}^{2-}$ .

**Oxidation and Ionization.**—If, in the last illustration, we write the equation ionically:  $\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{++} + \text{H}_2$ , we discover that, logically, we must consider the change from metallic zinc to zinc-ion to be in itself oxidation. This is the case whether the zinc-ion later combines with a negative ion to form a molecule or not. Mere union or disunion of ions is neither oxidation nor reduction. Conversely, the discharge of the  $2\text{H}^+$  giving  $\text{H}_2$  is reduction.

Thus, ionization of an elementary substance to form a positive ion is oxidation, and ionization to form a negative ion is reduction, and conversely.

**Oxidation and Electrons.**—Increasing the valence of an atom of a positive element (oxidation) consists in removing one or more electrons:  $\text{Na}^0 - e = \text{Na}^+$  (p. 354). Increasing the valence of an atom of a negative element (reduction) means adding one or more electrons:  $\text{Cl}^0 + e \rightarrow \text{Cl}^-$ .

Hence, oxidation is removing electrons and reduction is adding electrons.

**Making Equations for Oxidations and Reductions.**—The writing of equations for actions involving oxidation and reduction, where there are more than two substances on one side of the equation, is difficult, and a system or plan is of great value. The plan of **partial equations** (p. 270) is often helpful. There are three other systems which are in use. (1) When the action involves oxygen acids and their salts, the formulæ can be rewritten so as to show the **anhydride** (see below). (2) The second, called the system of **positive and negative valences**, is more generally applicable (next section). (3) The third describes oxidation in terms of **ions and positive electrical charges** (p. 496).

**Making Equations: Using Positive and Negative Valences** (p. 425).—1. Each compound is composed of *elements* which are,

relatively to one another, *either positive or negative*. Thus, in  $\text{KMnO}_4$ , K and Mn are positive and O is negative. In  $\text{CS}_2$ , C is (relatively) positive and S negative. We say, then, that C has a positive valence of four (+4) and S has a negative valence of two (-2), just as it has in  $\text{H}_2\text{S}$ .

2. *In every compound, the algebraic sum of the positive and negative valences must be zero*. Thus, in  $\text{CS}_2$  the sum is  $+4 - 2 \times 2 = 0$  ( $\text{C}^{++}\text{S}_2^{--}$ ). This is simply the rule of equi-valence (p. 136), with the addition of the idea of relative positiveness and negativeness.

This enables us to **determine the valence of each element in a compound like  $\text{KMnO}_4$** .  $\text{K}^+$  is always univalent and positive.  $\text{O}^-$ , in inorganic compounds, is always bivalent and negative. The valence of Mn has different values:  $\text{Mn}^{\text{II}}\text{Cl}_2$ ,  $\text{Mn}_2^{\text{III}}\text{O}_3$ ,  $\text{Mn}^{\text{IV}}\text{O}_2$ ,  $\text{Mn}_2^{\text{VII}}\text{O}_7$ , etc. By the rule (sum of valences equals zero) we can tell the valence of Mn in this compound. The valence of  $\text{O}_4$  ( $4\text{O}^-$ ) is -8. That of K is +1. That of Mn must therefore be +7 ( $\text{KMn}^{+\text{VII}}\text{O}_4$ )\*. Again, in  $\text{HClO}_3$ , the valence of  $\text{O}_3$  is -6, that of H is +1, therefore that of Cl must be +5. Still again, in  $\text{K}_2\text{Cr}_2\text{O}_7$ , the valence of  $\text{O}_7$  is -14, that of  $\text{K}_2$  is +2, that of  $\text{Cr}_2$  is therefore +12, and that of Cr necessarily +6 ( $\text{K}_2\text{Cr}_2^{+\text{VI}}\text{O}_7$ ).

3. Since rule 2 applies to every compound used or produced in a chemical change, it follows that when in a reaction *the valence of an element changes in value, that of one or more of the other elements must also change, so as to maintain the equality of + and - valences*. Thus, if one element loses in valence, to the extent of +6, some other element (or elements) must lose -6, or gain +6. The gain (or loss) of one element must cancel the gain (or loss) of some other element.

4. *The valence of a free element, that is, its active valence, is zero*. A free element is also *neutral* — neither positive nor negative — because it is not combined with any other element.

*Illustration of rules 3 and 4*. Thus, in the action for preparing chlorine with manganese dioxide (p. 219):



$4\text{H}$  ( $4\text{H}^+$ ) has the valence +4 on both sides. On the left side,  $4\text{Cl}$  ( $4\text{Cl}^-$ ) has the valence -4: on the right  $2\text{Cl}$  has the valence -2, and  $\text{Cl}_2$  has the valence 0. So far as chlorine is concerned,

\* The reader should write this, and other formulæ discussed below, so as to show the valences thus:  $\text{K}^+\text{Mn}^{++++}\text{O}_4^{--}$  (cf. p. 425).

there is a change from  $-4$  to  $-2$ , or a difference of  $-2$ . Again, on the right, Mn has the valence  $+2$ , while on the left side it has the valence  $+4$ , a difference of  $+2$ . The two differences,  $-2$  and  $+2$ , cancel one another. Stated otherwise, manganese lost  $+2$  and chlorine lost  $-2$ , so that the other  $+$  and  $-$  valences *still in use* remained equal in number, and equi-valence was preserved.

*Balancing an Equation.* Suppose we wish to balance the equation for the decomposition of chloric acid  $\text{HClO}_3$ . We ascertain, in the laboratory, that the products are perchloric acid  $\text{HClO}_4$ , chlorine dioxide  $\text{ClO}_2$ , and water.

*Skeleton:*  $\text{HClO}_3 \rightarrow \text{HClO}_4 + \text{ClO}_2 + \text{H}_2\text{O}$ .

Since  $\text{H}^+$  and  $\text{O}^-$  do not change in valence, only Cl has been affected. On the left side, the valences are  $\text{O}_3 = -6$ ,  $\text{H} = +1$ , Cl therefore  $= +5$ .\* On the right side, in  $\text{HClO}_4$ , the total valence of oxygen is  $-8$  and of hydrogen  $+1$ . That of Cl is therefore  $+7$ . In  $\text{ClO}_2$ , the valence of  $\text{O}_2$  is  $-4$ , and that of Cl therefore  $+4$ . Thus, Cl changes, from  $+5$ , partly to  $+7$  and partly to  $+4$ . To achieve this, arithmetically, we require  $3\text{Cl}$  on the right ( $= 3 \times +5 = +15$ ), giving  $\text{Cl} = +7$  and  $2\text{Cl} = 2 \times +4 = +8$ , or a total of  $+15$  on the left. Thus, we require  $3\text{HClO}_3$ :

*Balanced:*  $3\text{HClO}_3 = \text{HClO}_4 + 2\text{ClO}_2 + \text{H}_2\text{O}$ .

*Balancing Another Equation.* In the reaction for preparing chlorine (p. 218), the skeleton is:

*Skeleton:*  $\text{KMnO}_4 + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{KCl} + \text{MnCl}_2 + \text{Cl}$ .

Here, in  $\text{KMnO}_4$ , the valence of Mn is  $+7$ . In  $\text{MnCl}_2$  it is  $+2$ , a loss of  $+5$ . The chlorine also changes its valence from  $-1$  to  $0$ , a loss of  $-1$ . Evidently, so that the changes may cancel out, for every Mn losing  $+5$ ,  $5\text{Cl}$  must lose  $5 \times -1$  and be liberated:

*Incomplete:*  $\text{KMnO}_4 + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{KCl} + \text{MnCl}_2 + 5\text{Cl}$ .

Since there is now, altogether,  $8\text{Cl}$  on the right,  $8\text{HCl}$  will be required on the left. The  $8\text{H}$  will give  $4\text{H}_2\text{O}$ :

*Balanced:*  $\text{KMnO}_4 + 8\text{HCl} \rightarrow 4\text{H}_2\text{O} + \text{KCl} + \text{MnCl}_2 + 5\text{Cl}$ .

*Molecular:*  $2\text{KMnO}_4 + 16\text{HCl} \rightarrow 8\text{H}_2\text{O} + 2\text{KCl} + 2\text{MnCl}_2 + 5\text{Cl}_2$ .

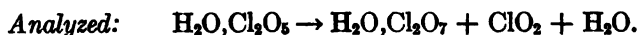
For another method of balancing this equation, see p. 496.

\* Write these (and other formulæ) thus:  $\text{H}^+\text{Cl}\ddot{\text{Cl}}^+\text{O}_3^-$  (cf. p. 425).

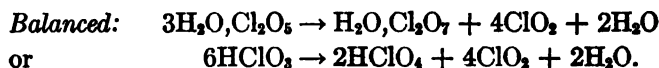
**Making Equations, by Using the Anhydrides.**—To balance the equation for the decomposition of chloric acid, we first write the skeleton equation:



Then we divide the acids into water and the anhydrides (p. 484).

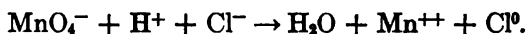


We now perceive that, disregarding the water, some  $\text{Cl}_2\text{O}_5$  must lose oxygen to give  $2\text{ClO}_2 + \text{O}$ , and that some  $\text{Cl}_2\text{O}_5$  must gain 2O, becoming  $\text{Cl}_2\text{O}_7$ . To furnish the 2O, clearly  $2\text{Cl}_2\text{O}_5$  is required, giving  $4\text{ClO}_2 + 2\text{O}$ , and a third  $\text{Cl}_2\text{O}_5$  gains this 2O. Thus, altogether  $3\text{Cl}_2\text{O}_5$  will be required:

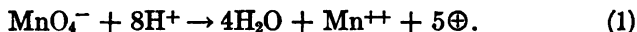


This equation is then divided by two throughout.

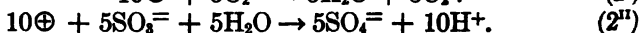
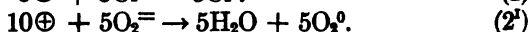
**Making Equations by Oxidation of Ions, Using Positive Electrical Charges.**—All oxidation reactions involving ionogens can be written in terms of ions. Thus, the oxidation of hydrochloric acid by potassium permanganate can be so written. The potassium-ion clearly is not affected, and may be omitted. The ions concerned are:



$\text{Cl}^0$  with no charge stands for free chlorine. Now we can divide the action into (1) the behavior of the oxidizing agent, which is general, and will be used wherever the same oxidizing agent is used; (2) the fate of the substance being oxidized, which again is general, because other oxidizing agents will change it in the same way.



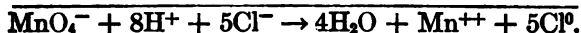
In words, each permanganate ion, with a free acid present (oxidizing mixture), will give water, manganous-ion, and a balance of five unit positive charges.



These three equations represent the oxidation of (2) hydrochloric acid, or (2') hydrogen peroxide, giving free oxygen, or (2'') sul-

phurous acid, with water furnishing the oxygen, and leaving the solution strongly acid ( $= 5\text{H}_2\text{SO}_4$ ). Note that the sums of the + and - charges on opposite sides of each equation are equal.

To obtain the final ionic equation, add (1) and (2):



Before adding (1) and (2') and (1) and (2''), the first equation (1) must be doubled throughout, so that the  $10\oplus$  may cancel out.

**Exercises.** — 1. Assign to its proper class (pp. 228, 402) each of the actions mentioned in this chapter.

2. Knowing that sodium acid tartrate  $\text{NaHC}_4\text{H}_4\text{O}_6$  is insoluble in 50 per cent alcohol, how should you make chloric acid (p. 482)?

3. Make the equation for the interaction of chlorine with calcium hydroxide in hot water (p. 480). How should you make zinc chlorate from zinc hydroxide  $\text{Zn}(\text{OH})_2$ ?

4. How should you make pure potassium hypochlorite from hypochlorous acid (p. 474)?

5. Explain, in terms of ionic equilibrium, why dilute hypochlorous acid can be obtained by adding one-half of an equivalent of an active acid (p. 475) to bleaching powder, and distilling the mixture.

6. On what circumstances would the possibility of making barium chlorate by action of chlorine on barium hydroxide depend (p. 481)? Could pure barium chlorate be obtained easily by this means (see Table of Solubilities)?

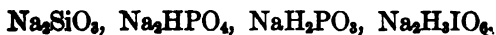
7. Make the equations for: (a) the preparation of potassium bromate; (b) pure aqueous bromic acid; (c) the interaction of iodine with aqueous potassium hydroxide in the cold, and (d) when heated.

8. Make the equations for the interactions of chlorine dioxide with water, and with aqueous potassium hydroxide.

9. Find the formulæ of the anhydrides of the following acids:



10. Find the formulæ of the anhydrides of the acids from the following formulæ of salts:





11. Classify the following changes as oxidations or reductions: (a)  $\text{H}_2\text{Cr}_2\text{O}_7 \rightarrow \text{H}_2\text{CrO}_4 + \text{CrO}_3$ ; (b)  $\text{HMnO}_4 \rightarrow \text{MnO}_2$ ; (c)  $\text{I}^0 \rightarrow \text{I}^-$ ; (d)  $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ .

12. Using positive and negative valences, determine whether each of the following formulæ is correct or incorrect:  $\text{Ca}(\text{MnO}_4)_2$ ,  $\text{Al}(\text{ClO}_4)_3$ ,  $\text{Na}_2\text{HIO}_6$ .

13. Apply each of the three methods (pp. 493, 496) of writing equations to the four following reactions: (a) chlorine-water on bromine; (b) chlorine-water on hydrogen sulphide, giving free sulphur; (c) potassium permanganate and free acid on hydrogen sulphide, giving free sulphur; (d) potassium dichromate and free acid (p. 418) on hydrogen sulphide, giving the chromic salt of the acid ( $\text{Cr}^{\text{III}}$ ) and free sulphur.

14. Explain why chlorine is much less soluble in a solution of sodium chloride than in water.

15. Why does light liberate oxygen from chlorine-water, but not from chlorine hydrate?

16. Why does a given weight of chlorine in the form of hypochlorous acid have twice as great a bleaching (or oxidizing) capacity as has the same weight of chlorine in chlorine-water?

17. What would be the result of leading chlorine monoxide gas into concentrated hydrochloric acid?

18. When bromic acid acts upon iodine (p. 486), why is  $\text{HIO}_3$  and not  $\text{Br}_2$  formed?

## CHAPTER XXIV

### THE ATMOSPHERE. THE HELIUM FAMILY

WE have seen that, to counterbalance the pressure of the air over a certain area, a column of mercury of the same diameter averaging 760 mm. in height is required. Let the section of the column be 1 sq. cm. Then the pressure of a column of air 1 sq. cm. in section, and extending so far from the earth as any downward tendency of the air exists, is equal to the weight of a column of mercury containing 76 c.c. of the metal. The weight of 1 c.c. of mercury being 13.6 g., this volume of the metal weighs 1033.6 g. This number represents therefore the pressure which is exerted by the air upon each square centimeter of the earth's surface. In ordinary units of measure, this is nearly fifteen pounds to the square inch.

A more vivid appreciation of the reality of this pressure may be obtained by noticing one of its effects. By boiling a small quantity of water in a tin can furnished with a narrow opening, we remove the whole of the air from its interior, displacing it by steam. While the boiling is in progress, we suddenly close the opening with a tightly fitting cork and remove the burner. While the steam was still issuing from the opening, its pressure was practically that of the atmosphere, and the can was subject to the same pressure inside and out. With the removal of the flame, however, the steam condenses, and the pressure on the interior is reduced to a minute fraction of its original value, while the pressure on the exterior is still the same (1 atmosphere). Under this pressure a vessel of ordinary tin-plate completely collapses [Lect. exp.].

*Components of the Atmosphere.* — There are three classes of **components** in the air. Those of the **first** class, oxygen, nitrogen, and the inert gases of the helium family, are present in almost **constant proportions**. Those of the **second** class are very **variable in quantity**, and include carbon dioxide, water vapor, and dust. Those of the **third** class, such as the sulphur dioxide in city air, are **accidental**.

*Components which are Constant in Amount.* — The determination of the **oxygen** by burning phosphorus in air, and measuring the residual gas, is not capable of application in an exact manner. A

stick of phosphorus, enclosed in wire gauze (Fig. 115), removes the oxygen rather slowly [Lect. exp.]. It is better to use a large amount of phosphorus in the form of thin wire. In this way a great surface is obtained, and the absorption of oxygen from a sample of air may be

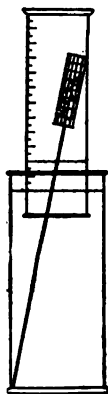


FIG. 115.

carried out in a few seconds. This method gives fairly accurate results, since there is no time for any appreciable change in the temperature or pressure of the atmosphere during the experiment. Several oxygen acids of phosphorus are formed. The passage of purified air over heated copper has also been used for the same purpose. When this method is employed, the volume of the nitrogen and argon which survives the action of the copper is measured, while the increase in weight of the copper, through formation of cupric oxide, gives the weight of the oxygen which was originally mixed with it.

Still another method, which is in constant employment in the analysis of mixtures of gases, may also be applied to the air. It consists in bringing a measured volume of air in contact with an alkaline solution of potassium pyrogallate, which quickly absorbs the oxygen, and noting the decrease in volume.

In the air taken from mines, from mountain tops, from the surface of the sea, and from inland regions, the proportion of oxygen to the residual gas is found to be fairly constant, although easily perceptible differences are noted. The percentage of oxygen in dried air ranges between 20.26 and 21.00, the latter being the proportion in normal air.

When the residual gas is led slowly through a heated tube containing magnesium, the nitrogen unites with the metal to form the solid nitride  $Mg_3N_2$ , and only about 10 c.c. out of every liter remains uncombined. This residuum is argon, mixed with 0.15 per cent of its volume of other gases belonging to the helium family (see below). Exact measurement by volume gives 78.06 per cent of nitrogen and 0.94 per cent of argon in dried air.

#### *Gaseous Components which are Variable in Amount.—*

Pure country air contains about 3 parts in 10,000 of carbon dioxide. In city air there are from 6 to 7 parts in the same volume, while in the air of audience-rooms, where the ventilation is defective, the proportion may rise as high as 50 parts.

The simplest way of showing the presence of carbon dioxide in the

air is by exposing a solution of barium hydroxide, an active base, in a shallow vessel. After a short time a layer of barium carbonate forms upon the surface:  $\text{Ba}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 \downarrow + \text{H}_2\text{O}$ . The same action may be utilized for the purpose of quantitative analysis. A measured volume of air is bubbled slowly through a measured volume of a solution of barium hydroxide of known concentration, and the quantity of barium hydroxide remaining is determined by titration (p. 390).

The **sources** of the carbon dioxide in the air are numerous. It comes from the decay of vegetable and animal matter, in which, chiefly through the influence of minute vegetable organisms, the carbon is oxidized to carbon dioxide. It is formed also by the combustion of coal and wood, but the thirteen hundred million tons of coal burned annually, giving three times that weight of carbon dioxide, would add only one-six hundredth to the total present in the air. It is exhaled by animals, being produced in the body by oxidation of the carbon in the food which they eat. It also issues from the earth, in volcanic as well as in other neighborhoods. The proportion of this gas in the air would naturally increase continuously, though slowly, as the result of these processes, were it not that it is removed just as continuously by the action of growing plants (see p. 579), which use it as food. It may be added, also, that carbon dioxide, being a soluble gas, is contained in sea water, dissolved and as  $\text{Ca}(\text{HCO}_3)_2$ , and the total amount in the ocean is much greater than that in the air. The removal by plants and by solution in sea water thus keeps the proportion in the air fairly constant.

The presence of carbon dioxide in the breath may be shown very quickly by blowing through a tube into calcium hydroxide solution (limewater). Calcium carbonate  $\text{CaCO}_3$  is precipitated. We draw about 500 c.c. of air into our lungs at each breath, or half a cubic meter per hour. In the lungs, some oxygen is removed, the percentage by volume falling from 21 to 16, and we add some carbon dioxide, the proportion increasing from 0.03 in country air to about 4 per cent. A candle flame is extinguished in exhaled air, because the maintenance of such a flame requires at least 18.5 per cent of oxygen. But air will sustain life until the proportion has fallen to about 10 per cent.

The proportion of **water vapor** is constantly changing. When the air becomes cool, as it does most often in the upper layers, the vapor condenses to droplets, forming fogs and clouds. When the condensation continues, the drops become larger and fall as rain. On

the other hand, when the weather is warm, water from the soil, and from rivers, lakes, and oceans, passes into vapor and the amount in the air increases.

The **ammonium nitrate** rises from the interaction of nitric acid and ammonia. The latter is formed by the decay of animal matter (p. 517); the former by the union of nitrogen and oxygen during thunder-storms. The electrical discharges produce nitrogen tetroxide (see p. 533), which with water gives nitric acid (*q.v.*).

**Humidity.** — The moisture in the air is usually defined in terms of the relative humidity, the standard being the quantity required to saturate the air. The open air is seldom actually saturated, but, when a portion is confined in a vessel over water, it soon becomes so. The humidity is then 100 per cent. If the partial pressure of water vapor present is only half as great as the vapor pressure of water at the same temperature, the humidity is 50 per cent. The average humidity of the atmosphere is roughly about 66 per cent.

At 18° (64.4° F.), the vapor pressure of water is 15.4 mm. Thus air saturated with moisture at 18° (100 per cent humidity) would contain 15.4/760, or about 2 per cent by volume of water vapor. If this air were cooled to 0° (32° F.), a temperature at which the vapor pressure of water is only 4.6 mm., the air could *retain* only 4.6/760, or 0.6 per cent, of moisture. The difference, amounting to 10.4 g. (10.4 c.c.) of water per cubic meter, would condense as fog or rain.

The proportion of water in a given volume of air may be measured most accurately by permitting the air to stream slowly through tubes filled with calcium chloride or phosphoric anhydride. The increase in weight of the charged tubes represents the quantity of moisture abstracted from the sample. It may also be ascertained by noting the temperature to which air has to be cooled before it becomes saturated and deposits dew (dew-point). For example, if air at 18° has to be cooled to 11° before it deposits dew, it contains water vapor at a pressure of 9.8 mm. (Appendix IV). If saturated at 18°, it would have contained water vapor at a partial pressure of 15.4 mm. The relative humidity was, therefore, 9.8/15.4, or 63.6 per cent.

**Ventilation.** — On a moist day, we speak of the atmosphere as "heavy" or "oppressive." The barometer, however, is lower on such days, and the pressure below the average. Moist air must

be lighter than dry air, because in moist air molecules of relative weight 18 ( $\text{H}_2\text{O}$ ) have been substituted for an equal number of molecules of oxygen and nitrogen with the relative weights 32 and 28. The discomfort is due to a different cause.

The oxidation of digested food carried by the blood is accompanied by liberation of heat, yet our bodies must remain at  $98.6^\circ\text{F}$ . ( $37^\circ\text{C}$ .). A rise of a few tenths of a degree produces discomfort. A little of the heat is lost by radiation from the surface of the body, but the real adjustment is secured by evaporation of water through the skin. The vaporization of 1 g. of water (at  $100^\circ$ ) removes heat amounting to 540 calories (603 cal. at  $37^\circ\text{C}$ .). Evaporation of a single ounce ( $28\frac{1}{2}$  g.) of water will therefore lower the temperature of 96.5 kilograms (168 lbs.) of water (or flesh, which is largely water) by two-tenths of a degree C. (nearly  $0.4^\circ\text{F}$ .).

The "oppressive" feeling, then, is due to the fact that the air is too nearly saturated, evaporation is being hindered (p. 147), and heat is accumulating. Hence, the relative humidity is the measure of the goodness or badness of the air of a room.

In winter, cold and therefore relatively dry air is brought into the house and heated. This makes the relative humidity very low, evaporation proceeds too fast, and discomfort follows. In summer, however, the outside air is often already nearly saturated at the temperature of the room. Unless there is a rapid change of air by ventilation, the moisture from the bodies of those in the room increases the humidity, and discomfort arises from a cause opposite to the one which produced it in winter.

It should be noted, also, that even though the air is in constant motion, the layer of air next our skin (even the exposed parts) is hindered from moving by friction. There is a **stationary layer** close to the surface, which quickly reaches the temperature of the body and becomes saturated at that temperature. The water molecules can leave this layer, and make room for others, only by *diffusion*, which is a deliberate rather than a speedy process. Now, an electric fan, although it brings no fresh, dryer air into the room, nevertheless stirs the air and blows away the moist, saturated layer next the skin. It, at least, makes this layer much thinner, and reduces greatly the distance the water molecules have to go by mere diffusion.\*

\* The same conception applies to **dissolving a salt**. A stationary layer of saturated solution is formed on the surface, and the molecules of the salt can escape, and make room for more, only by diffusion. In liquids, this is a *very*

Formerly, the accumulation of carbon dioxide from the breath was blamed for the unhealthiness of unventilated rooms. The proportion found in such rooms, however, is almost never sufficient to do any harm. Then, it was imagined that traces of highly poisonous compounds were exhaled by the body. No one, however, has yet been able to prove that such poisons exist.

The aims of ventilation are, therefore, to supply fresh outside air, to keep it in motion, and to maintain a humidity that is neither too low nor too high.

**Dust in the Air.** — A beam of sunlight, crossing a dark room, can be seen by the light reflected from the particles of dust in the air. The dust varies both in kind and quantity according to the locality. It is found to be partly **inorganic**, and to consist of clay, limestone, and soot from ill-burned fuel. In factories the dust may consist of minute particles of glass, steel, cement, or other substances. The **organic** dust may be divided into two kinds. The part which is dead includes coal dust, refuse from the streets, minute shreds of cotton, linen, hay, etc. The living dust consists of pollen grains, spores of fungi and molds, bacteria, and similar microscopic organisms. The presence of such germs in the air is shown by the fact that, when nutritive liquids have been exposed to the air, even for a few minutes, putrefaction very soon sets in. Some germs also produce disease when they land on a place where the skin has been damaged by a cut or burn, or on an incision made in the course of an operation. After infection, antiseptic treatment, *e.g.*, with hydrogen peroxide, destroys the organisms. But protection in advance, *e.g.*, with petrolatum (*q. v.*), until a new skin has formed, is better.

It is worth noting that natural soil contains about 100,000 micro-organisms per c.c., good, unfiltered river water from 6000 to 20,000 per c.c., and pure air only 4 or 5 per liter.

Flasks can be filled with dustless air through the displacement of that which they contain by air drawn through a wide tube packed with 12–15 inches of cotton. It has been shown by Aitken that air filtered in this way behaves differently from ordinary air in respect to the manner in which its moisture condenses.

If a sample of moist air is cooled until it contains more water vapor than it could take up at the existing temperature, the excess of moisture slowly process. By shaking the solid and liquid, however, the stationary layer is partly washed away. It is made thinner, so that the distance the molecules have to travel by diffusion is greatly reduced, and the whole operation is hastened.

ture is deposited. This deposition usually takes place by the formation of a multitude of little particles of liquid water, which together make up a fog. Now dustless air lacks this property entirely. When saturated with water and then cooled, it does not give any trace of fog. The excess of moisture is gradually deposited upon the walls of the vessel and upon any material objects which it contains, but of fog there is no trace visible. It seems that the particles of dust are required as nuclei round which the water may gather. In the absence of dust, and therefore of proper nuclei, the moisture is not precipitated in the usual way. Thus fogs and rain would be impossible but for the presence of dust in all ordinary air. In the absence of dust, the cooling would produce supersaturation, which would be slowly relieved by condensation on the surfaces of houses, plants, animals, and land. Thus, in a dustless atmosphere an awning or umbrella would afford no shelter.

The formation of fog in ordinary air, and its absence in filtered air, is easily shown in a darkened room (Fig. 116). The flask contains some water to saturate the air. When suction is applied, by the mouth, to the tube S, the

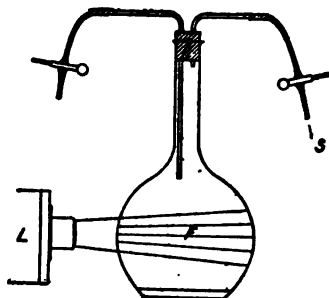


FIG. 116.

saturated air in the flask expands and is cooled.\* With ordinary air, a fog, brilliantly illuminated by the beam of light, is instantly produced. Filtered air (dustless) gives no fog. On the other hand, a whiff of smoke from smoldering paper, when admitted to the flask, causes a fog (after cooling) of extraordinary denseness [Lect. exp.].

By diluting air with dustless air, generating fog in the mixture, and, with the help of a microscope, counting the globules when they settle, an estimate of the number of particles of dust in air may be made. It is found that rain removes a large proportion of them, while respiration and combustion greatly increase their number. The prevalence of fogs in cities is thus accounted for. The following are the numbers of dust particles in 1 c.c. of air:

Outside, raining . . . . .	32,000	A room, near the ceiling . . . . .	5,420,000
Outside, fair . . . . .	130,000	Air above Bunsen flame . . . . .	30,000,000
A room . . . . .	1,860,000		

\* Compression with a bicycle pump *heats* air, and expansion cools it.



**Air a Mixture.**— Since the main components of air were not definitely identified until the end of the eighteenth century, we can understand why the substance was for long considered to be an element. The experiments which we have described, in which the oxygen was removed from the air and the nitrogen remained, do not prove that the original constituents were present simply in mechanical mixture. They might have been combined, and the combustion of phosphorus, for example, might have represented the removal of oxygen from combination with nitrogen and its appropriation by the phosphorus. It may be well, therefore, to point out some reasons which lead us to regard the air as a mixture:

1. When two substances enter into chemical combination, the new body invariably has different physical properties from either of the original ones. Each of the substances in air, however, has precisely the same properties which it exhibits when free, separate, and pure. This is characteristic of a mixture. Thus, there is no simple relation between the *refractive power* for light which a compound possesses and the refractive powers of its constituents. In the case of air, however, the refractive power is exactly that which we should calculate from the refractive powers of the constituents, taking into account the proportions of them which air contains.

Again, the nitrogen and oxygen *dissolve* independently in water in proportion to their solubilities and partial pressures (p. 189). If the air were a compound, it would dissolve as a whole, and the relative proportions of the components would not be changed by the process. Also, the *density* of air is precisely that which we find by calculation from the known proportions and several densities of the components. Likewise, when liquefied air is allowed to evaporate in a suitable apparatus, the nitrogen, being more volatile, can be separated from the oxygen. When the oxygen, in turn, is allowed to evaporate, the carbon dioxide and water remain as solids, frozen at this low temperature. No compound of nitrogen and oxygen is found.

2. The proportion by volume in which the gases are found in the air is not so simple as the proportions which we observe in cases of chemical combination. The proportion is close to 4 : 1, but not exactly 4 : 1. Besides, as we have seen, the proportion is not perfectly constant.

3. The composition of air varies, while the composition of definite chemical substances is always the same. The proportions by weight also in which the components are contained in air are not integral multiples of the atomic weights (see Exercise 2).

**Composition of Air.** — Air, when freed from carbon dioxide and water, contains by volume 78.06 per cent of nitrogen, 21.00 per cent of oxygen, and 0.94 per cent of argon. When only the water is removed, the carbon dioxide averages about 0.03 per cent of the whole.

To use an illustration of Graham's, if we imagined the air to be divided by magic into layers, all at one atmosphere pressure, and with the heavier components below, we should have: On the earth, five inches of water; above that, thirteen feet of carbon dioxide; above that, ninety yards of argon; above that, one mile of oxygen; and on the top four miles of nitrogen.

**Liquefaction of Gases.** — The earliest experiments of this kind seem to have been made by Northmore (1805), who liquefied chlorine, hydrogen chloride, and sulphur dioxide. In 1823 chlorine was again liquefied by Faraday; and in the same year Davy, whose assistant Faraday was, liquefied hydrogen chloride. During the following years Faraday reduced other gases — sulphur dioxide, hydrogen sulphide, carbon dioxide, nitrous oxide, cyanogen, and ammonia — to the liquid condition. He failed, however, with oxygen, hydrogen, and nitrogen.

The method which he employed was extremely simple. He used a bent tube shaped like an inverted v ( $\Lambda$ ), into one limb of which materials for producing the gas were introduced (Fig. 90, p. 226). The other limb was then sealed up and immersed in a freezing mixture. The gas, usually liberated by heating, was liquefied by its own pressure in the cold limb. By means of a more elaborate apparatus, Cailletet and Pictet simultaneously (December, 1877) obtained, the one, a fog, and the other, a spray containing droplets of liquid oxygen. In 1883 Wroblevski and Olszewski made visible amounts of the same liquid. About the same time Dewar devised means of manufacturing large quantities of liquid air and oxygen.

The principle now used in liquefying gases depends on the fact that, although a *perfect* gas, when expanding into a vacuum, should suffer no fall in temperature, since it does no work, ordinary gases do become cooled very slightly. The work which they do in expanding in such circumstances is done in overcoming the cohesion between their molecules (p. 164), so that a tearing apart of the substance, which consumes heat, has to take place. Since this cohesion becomes more conspicuous the lower the temperature (*cf.* p. 166), the cooling effect of expansion becomes greater and greater as the temperature falls.

The most successful apparatus for use on a small or large scale is that devised by Hampson. In this apparatus (Fig. 117), two concentric copper pipes, about 130 meters in length, are coiled closely in a cylindrical form, with non-conducting covering to prevent access of heat from the outside. Air at 130–150 atmospheres pressure is forced through the inner pipe (upper opening, Fig. 117). When it reaches the extremity of this pipe, it suddenly escapes into a closed vessel. This expansion lowers its temperature. A spiral partition

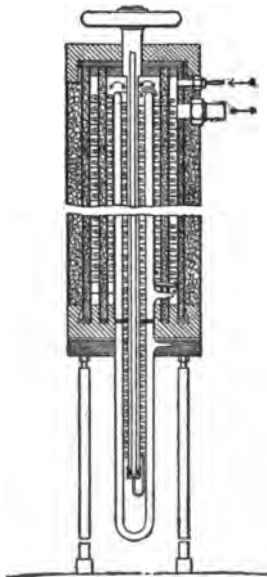


FIG. 117.

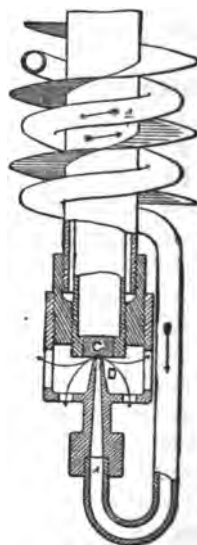


FIG. 118.

between the coils produces the outer tube of which we have spoken. The gas in the tube *A* (Fig. 118) is under a pressure of 130–150 atmospheres. The distance of the nozzle *D* from the plug *C* is adjusted so that the pressure of the gas in the chamber and spiral outer tube is reduced to one atmosphere. The air can now escape only by traveling back through the outer pipe to the final, wider exit near the top. In doing so, it cools the highly compressed air in the inner pipe. The cooler air, on reaching the closed vessel, expands and becomes colder than ever, and in passing backwards lowers the temperature of the air in the inner pipe still further. Finally, the air in this pipe liquefies, and drops of liquid air are expelled into the

closed vessel. This is allowed to run out through a valve, from time to time, as it accumulates.

Liquid air can be kept in Dewar flasks (Fig. 119). The space between the inner and outer flasks is evacuated, so that there is no gas to carry heat from the atmosphere in to the liquid air. The inner surface of the outer flask is often silvered, so that radiant heat, from surrounding bodies, may be reflected and not absorbed.

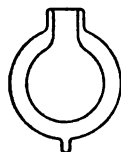


FIG. 119.

**Liquid Air.** — Liquid air varies in composition, as the nitrogen (b.-p.  $-194^{\circ}$ ) is less condensable than the oxygen (b.-p.  $-181.4^{\circ}$ ). It boils at about  $-190^{\circ}$ , and contains about 54 per cent of oxygen by weight, while air contains 23.2 per cent. By allowing evaporation to go on, a liquid containing 75 to 95 per cent of oxygen is easily obtained (cf. p. 81). The gas secured by the evaporation of the residue is pumped into cylinders and sold as compressed oxygen. It contains about 3 per cent of argon, and is a convenient source of this element. Cartridges made of granular charcoal and cotton waste, when saturated with liquid air, have been used as an explosive in mining.

### THE HELIUM FAMILY

**Argon A.** — Lord Rayleigh was the first to observe that, while specimens of oxygen and other gases made purposely from various sources always had the same density, nitrogen was an exception. One liter of nitrogen made from air, and supposed to be pure, weighed 1.2572 g. When the gas was manufactured by decomposition of five different compounds, such as urea and certain oxides of nitrogen, the results agreed well amongst themselves. But the mean weight of a liter of this nitrogen was only 1.2505 g. The difference, amounting to nearly 7 mg., was very much greater than the experimental error. The suspicion naturally arose that some heavier gas was present in atmospheric nitrogen. Soon after (1894), the late Sir William Ramsay, working in coöperation with Lord Rayleigh, obtained argon by removal of the greatly preponderating nitrogen by means of magnesium (p. 514). The new gas had a molecular weight of about 40, and was therefore more than one-third heavier than nitrogen.

In order to make sure that this substance did not have its source in the magnesium, a different method was used by Lord Rayleigh to separate it from nitrogen.

He inclosed the nitrogen with a sufficient quantity of oxygen in a flask, through the sides of which platinum poles had been inserted. A tube entered the flask by the neck, and through this a constant fountain of potassium hydroxide solution played upon the interior and kept the surface covered with fresh quantities of the liquid. Another tube permitted the overflow of the excess of this solution. The discharge of electricity produced nitrogen tetroxide (*q.v.*), which was absorbed by the potassium hydroxide to form potassium nitrate and potassium nitrite. The volume of gas thus continually diminished and, by persistent sparking of the mixture with oxygen, the nitrogen was finally all taken out. The excess of oxygen was then removed, and the gas which remained was found to be identical with that which Ramsay had obtained.

Lord Rayleigh's method was extremely interesting, since it was a reproduction of an experiment made by Cavendish more than one hundred years before (1785). The latter had remarked that the assumption that the inert atmospheric gas was a homogeneous single substance had not been confirmed by sufficiently careful experiment. He even endeavored in precisely the above way to remove the nitrogen in order to see whether any other body remained. He records the fact that only about 0.8 per cent of inactive gas remained. Since the quantity was so small, and the spectroscope, by which the gas even in small amounts would have been recognized to be new, was not invented until much later, he did not pursue the subject. Argon thus narrowly escaped detection over a century before its actual discovery.

The exact density of argon, referred to oxygen = 32, is 39.88. When liquefied it boils at  $-186.9^{\circ}$ , and the colorless solid, obtained by cooling the liquid, melts at  $-189.5^{\circ}$ . The solubility of the gas in water (4 volumes in 100) is two and one-half times that of nitrogen. It has not been found to enter into any sort of chemical combination, and was named argon on this account (Gk. *ἀργος*, inactive).

Since the atomic weight of a substance is a quantity showing the proportion in which it enters into combination, it will be seen that argon, since it has not yet been found to combine with anything, has, to speak strictly, no atomic weight (pp. 243, 254). At the same time, it is manifestly a question of interest to determine whether the physical properties require the supposition that the molecule of argon contains one atom, or more than one atom.

If gases were composed of perfectly elastic spheres, the molecules would be altered only in respect to velocity of movement by heating. Calculation enables us to determine that to raise the temperature of one G.M.V. of *such a gas* by one degree would require 3 calories in every case. Now Regnault found the following values (in calories) for the heat capacity of gases:

Oxygen (O <sub>2</sub> ) . . . . .	4.96	Carbon dioxide (CO <sub>2</sub> ) . . . . .	7.56
Hydrogen (H <sub>2</sub> ) . . . . .	4.82	Sulphur dioxide (SO <sub>2</sub> ) . . . . .	7.82
Nitrogen (N <sub>2</sub> ) . . . . .	4.82	Chloroform (CHCl <sub>3</sub> ) . . . . .	16.55
Hydrogen chloride (HCl) . . . . .	4.76	Alcohol (C <sub>2</sub> H <sub>5</sub> O) . . . . .	18.70

These gases evidently are not constituted as the hypothesis with which this paragraph opened supposes. Some heat is consumed in work done *inside* the polyatomic molecules, and the amounts by which the numbers exceed 3 calories show that the intramolecular work is greater as the complexity of the molecules increases. Now, in mercury vapor the value is exactly 3, and its vapor is monatomic (p. 250), so that in its molecules there is no opportunity for the consumption of heat in intramolecular change. Hence, when argon was found likewise to give 3 for the value of its molecular heat-capacity, identity of its atomic and molecular weights was demonstrated.

**Helium He.** — In 1868 Lockyer first detected an orange line in the spectrum of the sun's prominences, which was not given by any terrestrial substance then known. The line was so conspicuous that it was attributed to the presence, in considerable quantity, of a new chemical element, which was named **helium** (Gk. *ἥλιος*, the sun). Ramsay, in searching for sources of argon, examined a gas which Hillebrand had obtained by heating uraninite, an ore of uranium. He was surprised to find (1895) that the gas was not nitrogen, as had been supposed, nor was it even argon. It frequently contained a large proportion of a gas, very much lighter than either, the spectrum of which showed at once that it was identical with helium. The same gas has since been obtained from other minerals, from the water of certain mineral springs, and it is found in small amount in the atmosphere. Helium does not exhibit any tendency to enter into combination, either with the elements which its parent minerals contain, or with any others. It is monatomic (*cf.* p. 510) and its density shows that its molecular weight is 4. When liquefied by Onnes, it boiled at  $-268.5^{\circ}$  ( $4.5^{\circ}$  abs.), and had a density of only 0.15.

**Neon Ne, Krypton Kr, Xenon Xe, and Niton Nt.** — When the argon obtained from atmospheric nitrogen was cooled with liquid air ( $-190^{\circ}$ ) by Ramsay (1898), the argon, krypton, and xenon were liquefied, and the neon and helium were dissolved by the liquid. When heat was allowed to reach the mixture, the last two gases escaped first, along with much argon. When most of the argon had

escaped, the krypton and xenon still remained liquid. By repeated liquefaction and fractional evaporation (see under Petroleum), the krypton and xenon were separated from the argon and from one another. When the vessel containing the mixture of helium and neon was immersed in liquid hydrogen ( $-240^{\circ}$ ), the second froze to a white solid, and the helium, which remained gaseous, could be pumped off. All these gases together constituted one-six hundredth part of the atmospheric argon.

These gases are all entirely inactive chemically, and are all monatomic. Their molecular weights are: Neon (Gk. νέος, new), 20.2; krypton (Gk. κρυπτόν, hidden), 82.92; xenon (Gk. ξένος, stranger), 130.2.

Niton (radium emanation, *q.v.*), molecular weight 222.4, also belongs to this family.

**Exercises.** — 1. A sample of moist air, confined over water at  $15^{\circ}$  and 760 mm., occupies 15 c.c. It is mixed with 20 c.c. of hydrogen, and the mixture is exploded, and suffers a contraction of 9.5 c.c. What would be the volume of the oxygen it contained if measured dry at  $0^{\circ}$  and 760 mm.?

2. Calculate, from the data on p. 500 and the densities, the percentage by weight of the three principal components of air.

3. Of the proofs that air is a mixture (p. 506), which show that *no part* of the components is combined, and which that the components are not *wholly* combined?

4. What is the relation between heavier clothing and the stationary layer of air next the skin?

5. From the data given on p. 502, calculate the weight of water vapor in 1 cubic meter of air saturated at  $18^{\circ}$  and at  $0^{\circ}$ , respectively.

## CHAPTER XXV

### NITROGEN AND ITS COMPOUNDS WITH HYDROGEN

NITROGEN was recognized to be a distinct substance by Rutherford (1772), Professor of Botany in the University of Edinburgh, who named it mephitic air. Scheele showed that it was present in the atmosphere. Lavoisier recognized it to be an element, and named it *azote* (Gk., *without life*) because it did not support life. The English name records the fact that it is an important constituent of saltpeter  $\text{KNO}_3$  (Lat. *nitrum*).

**The Chemical Relations of the Element Nitrogen.**—In compounds with hydrogen and the metals nitrogen is trivalent, while in those containing oxygen and other negative elements it is frequently quinquivalent. It is a non-metal, for its oxides are acidic (p. 150). Many of the compounds of nitrogen are extremely active and interesting. Those of them which we have to discuss in inorganic chemistry are ammonia  $\text{NH}_3$  and nitric acid  $\text{HNO}_3$ , and several related substances. The organic compounds containing nitrogen are very numerous and possess highly characteristic properties. Some, like nitroglycerine (*q.v.*) and guncotton, are violently explosive; others, like antipyrine, show great physiological activity; still others, such as the aniline and other organic dyes, provide us with beautiful and useful coloring matters.

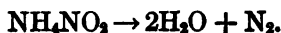
**Occurrence.**—Apart from the presence of free nitrogen in the air, the element is found in many forms of combination. The nitrates of potassium and sodium are found in Bengal and other tropical countries and in Chile, respectively. Natural manures, such as guano, contain large quantities of nitrogen compounds, and owe their value as fertilizers to this fact. Nitrogen is an essential constituent of the proteins (about 16 per cent nitrogen) of vegetable and animal matter.

**Preparation.**—Nitrogen containing about one per cent of argon (*q.v.*) is easily obtainable from purified air, when the oxygen of the



latter is removed, for example, by passage over heated copper. For commercial purposes, it is obtained by evaporation of liquid air.

When pure nitrogen is required, it must be obtained from chemical compounds, in order that it may be free from argon. The simplest method is to heat ammonium nitrite:



In practice, since ammonium nitrite is unstable and cannot easily be kept, a mixture of an ammonium salt with some salt of nitrous acid is employed. Thus, when strong solutions of ammonium chloride and sodium nitrite are mixed, a double decomposition results in the formation of ammonium nitrite,  $\text{NH}_4\text{Cl} + \text{NaNO}_2 \rightleftharpoons \text{NH}_4\text{NO}_2 + \text{NaCl}$ , and this breaks up when heat is applied, giving nitrogen.

We may also prepare nitrogen by the oxidation of ammonia  $\text{NH}_3$  by passing the latter over heated cupric oxide (see p. 519), or by the reduction of nitric oxide  $\text{NO}$  by passing this gas over heated copper.

**Physical Properties.** — Nitrogen is a colorless, tasteless, odorless gas, as we should expect from the fact that air possesses these properties. It forms a colorless liquid, boiling at  $-194^\circ$ . By further cooling, this liquid freezes to a white solid (m.-p.  $-214^\circ$ ). The solubility of nitrogen in water (1.6 vols. in 100) is less than that of oxygen.

**Chemical Properties.** — The density of the gas shows the formula of free nitrogen to be  $\text{N}_2$ .

Nitrogen *unites* with few common chemical elements directly. At ordinary temperatures it is almost absolutely indifferent. When passed through a tube over strongly heated lithium, calcium, magnesium, or boron, it forms definite chemical compounds, known as *nitrides*, in which it is trivalent. These have the formulæ  $\text{Li}_3\text{N}$ ,  $\text{Ca}_3\text{N}_2$ ,  $\text{Mg}_3\text{N}_2$ , and  $\text{BN}$ , respectively. Thus, when magnesium is burned in the air, the white mass which is formed contains magnesium nitride, along with much of the oxide. When the ash is moistened with water in a covered vessel, ammonia can be smelt and can be detected with moist litmus paper [Lect. exp.]. The nitride is hydrolyzed:



Nitrogen combines with difficulty with hydrogen to form ammonia  $\text{NH}_3$  and with still greater difficulty with oxygen to form nitric oxide  $\text{NO}$ . The actions will be discussed under the compounds themselves.

The indifference of free nitrogen is doubtless due to the fact that its molecules  $N_2$  are extremely stable.

One case of direct union of nitrogen is of economic importance. The supply required by plants is obtained partly from nitrogen compounds contained in fertilizers, or equivalent substances already present in the soil. The *leguminosæ*, such as peas, beans, clover, and alfalfa, are associated constantly with certain bacteria which flourish in nodules upon their roots. These bacteria have the power of taking free nitrogen from the air, which penetrates the soil, breaking up its molecules, and producing proteins. The nodules often contain over five per cent of combined nitrogen. The proteins, by the action of nitrifying bacteria, give nitric acid which, with bases in the soil, gives nitrates. These are soluble, and are absorbed through the roots, furnishing the nitrogen needed by plants to enable them to construct the proteins they require.

An active form of nitrogen, discovered by Strutt, is produced by passing an electric discharge through the gas under low pressure. When the discharge is stopped, a yellow light is produced by the reversion of the nitrogen to the inactive form. A trace of oxygen seems to be required, possibly as a catalyst. With a little vapor of pentane  $C_5H_{12}$  in the tube, this active nitrogen gives hydrocyanic acid  $HNC$  (*q.v.*).

**Compounds of Nitrogen and Hydrogen.**—The commonest and longest known of these substances is ammonia  $NH_3$ , which was first described by Priestley (1774) and named "alkaline air." Curtius discovered hydrazine  $N_2H_4$  in 1889, and hydrazoic acid  $HN_3$  in 1890. Hydroxylamine  $NH_2O$ , discovered by Lossen in 1865, is similar to ammonia in chemical behavior.

#### AMMONIA $NH_3$

Ammonia is of interest, commercially, because large amounts of liquefied ammonia are used in refrigeration, because much is employed in the manufacture of carbonate of soda, and because its compounds are used as fertilizers.

**Manufacture.**—Ammonia is formed when proteins are heated in the absence of air. Thus, it was formerly obtained by the distillation of hoofs, hides, and horns, and the solution in water was called "spirit of hartshorn." Coal contains 1-2 per cent of combined

nitrogen, derived from the proteins of the original plants. Hence, when coal is distilled in the manufacture of coal gas or, on a much larger scale, for the making of coke, much ammonia can be secured by washing with water the gases which are given off. The solution is separated from the tar, lime is added to liberate the ammonia, and the ammonia gas is driven out by heating and passed into sulphuric acid or hydrochloric acid. It gives ammonium sulphate or chloride (see below).

In Germany 80 per cent (1910) of the coke is made in "by-product" coke ovens, in which the ammonia and other by-products are collected and utilized; in the United States 83 per cent of the coke is made in "beehive" ovens (1911) in which the vapors are simply burned. Ammonium sulphate is a valuable fertilizer and in 1911, in the United States, ammonia capable of yielding 400,000 tons of ammonium sulphate worth 24 million dollars was burned by the cokemakers.

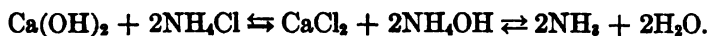
The distillation of coal is the chief source of commercial ammonia. In Scotland, however, oil-bearing shale is distilled to obtain petroleum, and much ammonia, liberated at the same time, is collected. Formerly it was allowed to escape but, in the absence of a protective tariff, the competition of American and Russian petroleum compelled economy. Now, the profit on the ammonium sulphate pays the whole cost of mining and distilling the shale.

**Synthetic Ammonia.**—The direct union of nitrogen and hydrogen (1 vol.: 3 vols.) to form ammonia:  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 + 2 \times 12,200 \text{ cal.}$  is a reversible reaction. Since heat is absorbed in decomposing ammonia, the proportion of this gas present at equilibrium becomes rapidly smaller as the temperature rises (van't Hoff's law, p. 305). The proportions (at 760 mm.), determined by Haber, are: 200°, 15.3 per cent; 300°, 2.2 per cent; 500°, 0.13 per cent; 700°, 0.02 per cent; 1000°, 0.004 per cent. Thus, at 700° ammonia is practically all decomposed, and at low temperatures the action is so slow that no union to form ammonia is perceptible.

The Badische Company is now (1914) manufacturing ammonia on a large scale, for the preparation of explosives, by the direct union of nitrogen and hydrogen. It is necessary to use a lower temperature and a contact agent—such as specially prepared iron—to hasten the action. Then, too, the reaction is accompanied by a diminution in volume (4 vols.  $\rightarrow$  2 vols.), and is therefore assisted by using the gases under a pressure of 185–200 atmospheres (Le Chatelier's law,

p. 307). Below  $500^{\circ}$ , with these conditions, about 8 per cent of the gases combine. The ammonia is dissolved out with water, and the uncombined gases are sent through the process again. The required hydrogen may be obtained by one of the commercial processes (p. 122), and the nitrogen from liquid air.

**Preparation in the Laboratory.** — 1. A mixture of slaked lime and some salt of ammonium, such as ammonium chloride, either with or without water, is heated in a flask or retort provided with a delivery tube:



The ammonium hydroxide, formed by the double decomposition, being unstable, immediately decomposes.

2. Warming the aqueous solution gives a steady stream of the gas. Since the gas is very soluble in water, it is collected over mercury or by downward displacement of air. The moisture which it contains is removed by passage through a tower or wide tube filled with quicklime. Calcium chloride cannot be used, as the gas combines with it forming a compound  $\text{CaCl}_2 \cdot 8\text{NH}_3$ , similar in properties to a hydrate (pp. 150–154).

In the decay of meat (containing proteins) and of manure, the strong odor is due in part to the ammonia produced.

**Physical Properties.** — Ammonia is a colorless gas with a pungent, characteristic odor familiar in smelling-salts. The G.M.V. of the gas weighs 17.26 g., so that the density is little more than half that of air (cf. p. 233). When liquefied it boils at  $-33^{\circ}$  and exercises a pressure of 6.5 atmospheres at  $10^{\circ}$  (density 0.62 at  $0^{\circ}$ ). The solid is white and crystalline (m.-p.  $-77^{\circ}$ ). The gas is very soluble in water, one volume of the latter dissolving 1300 volumes of the gas at  $0^{\circ}$ , 783 volumes at  $16^{\circ}$ , and 306 volumes at  $50^{\circ}$ . The 35 per cent aqueous solution, saturated at  $15^{\circ}$ , and sold as "concentrated ammonia," has a sp. gr. 0.881. The whole of the dissolved gas may be removed by boiling (cf. p. 211).

Liquefied ammonia is used in refrigeration. In evaporating at  $-33^{\circ}$  it absorbs 330 cal. per gram. Water alone has a greater heat of vaporization. The large amount of heat is, in both cases, required because of the relatively large volume of the vapor (due to low molecular weight) and to the fact that both liquids are associated (p. 282), and the complex molecules  $(\text{NH}_3)_2$  and  $(\text{NH}_3)_3$  have to be

decomposed. To freeze 1 gram of water at  $0^{\circ}$ , 80 cal. have to be removed. Thus 1 g. of liquid ammonia will convert 4 g. of water into ice. Fig. 120 shows one arrangement diagrammatically. The ammonia gas, obtained from a cylinder of liquid ammonia, is driven by the pump *F* along the tube *E* and is liquefied in the tube coiled in the tank *AB*. Cold water circulating through *AB* removes the heat produced by the compression and liquefaction of the gas. The liquid ammonia is allowed to drip through the stopcock *G* into the lower coil, and there it evaporates. In doing so, it takes heat from a 30 per cent solution of calcium chloride in water. This cooled brine leaves the tank at *D*, circulates through another tank, in which water-filled ice molds are suspended, and returns to *C*. When used for cooling storage-rooms for meat, the brine circulates through pipes in the same way. The machine is constructed of iron, because

copper and brass are corroded by ammonia.

**Chemical Properties.**—Ammonia, as we have seen (p. 516), is **not stable**, and decomposes almost completely at  $700^{\circ}$ . A discharge of sparks from an induction coil (temperature about  $2000^{\circ}$ ) has the same effect, so that a sample of the gas, confined over mercury in a closed tube (Fig. 121), may be shown to double in volume. Every two molecules give four:



That, even at this temperature, the action, being reversible, is still incomplete, can be shown by introducing a few drops of dilute sulphuric acid. The trace of ammonia remaining combines with this acid, forming  $(\text{NH}_4)_2\text{SO}_4$  in solution. If the discharge is continued, further traces of ammonia are formed and absorbed, until, finally, the whole gas disappears. The action, therefore, first goes almost completely in one direction, and then quite completely in the other, while no change has taken place in the conditions to which the gas

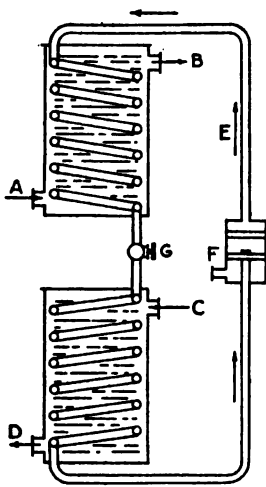


FIG. 120.

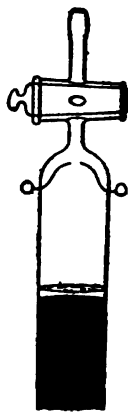


FIG. 121.

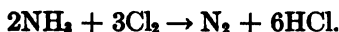
is subjected at the point where the interaction is occurring. The sole difference is that a little of an acid has been introduced into a relatively remote part of the space.

Ammonia **reduces** many oxides, when the latter are heated and the gas is led over them:



Ammonia burns in pure oxygen (not in air) to give steam and nitrogen. In air, heat is used up, not only in decomposing the compound, but also in raising the temperature of the nitrogen of the atmosphere. This causes a continuous drain on the heat given out by the action, and prevents the maintenance of the kindling conditions (p. 95).

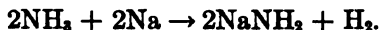
**Chlorine** and bromine (vapor) combine with the hydrogen and liberate nitrogen:



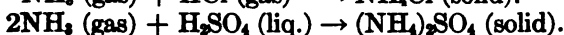
When **metals** capable of uniting with nitrogen (p. 514) are heated in a stream of ammonia gas, hydrogen is displaced. Magnesium gives magnesium nitride:



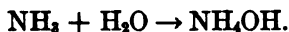
Sodium and potassium, however, give **amides** (compounds containing the group  $\text{NH}_2$ ), such as sodamide  $\text{NaNH}_2$ :



The most striking property of ammonia is that it **combines with acids**, giving ammonium salts:



It **combines also with water** at or below  $-79.3^\circ$  to give ammonium hydroxide as a white solid:

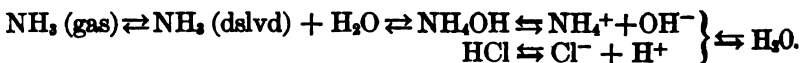


Since the solid liquefies above  $-79.3^\circ$ , a solution of the substance, which is contained in the aqueous solution of ammonia, is the only available form of ammonium hydroxide. In solution, it is a weak base. Ammonium oxide  $(\text{NH}_4)_2\text{O}$ , a solid, can also be formed below  $-78.6^\circ$ .

**Ammonium Compounds.**—Since  $\text{NH}_4$  plays the part of a metallic element, entering into the composition of a base and of

a series of salts, it is named **ammonium**. As this radical forms a univalent, positive ion  $\text{NH}_4^+$  and gives a distinctly alkaline base, it is classed with potassium and sodium as one of the metallic elements of the alkalis (*q.v.*).

**Ammonium Hydroxide  $\text{NH}_4\text{OH}$ .** — Although much less completely ionized than is potassium hydroxide, ammonium hydroxide affects litmus easily. In a normal solution 0.4 per cent of the ammonia is in the form of ammonium-ion  $\text{NH}_4^+$ . When an acid is added to the solution, the correspondingly small amount of hydroxide-ion which exists in it is removed, and the various equilibria are displaced forwards. The final result is the same as with any other base:



Only a small proportion of the gas (one-third) is actually combined at any one time, the greater part being simply dissolved.

The solution is sold as **household ammonia**, and is used, in washing and cleaning, to soften the water.

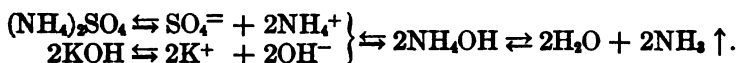
**Salts of Ammonium.** — When strongly heated, all ammonium salts are decomposed and many, *but not all*, give ammonia and the acid. When the latter is volatile, the whole material of the salt is thus converted into gas. If the acid is volatile without permanent decomposition, it reunites with the ammonia to form the solid salt when the vapor reaches a cool part of the tube (sublimation, p. 275):



This behavior distinguishes ammonium salts from those of the typical metals, for, with the exception of mercury salts, most other salts are not easily and completely volatilized. The use of ammonium chloride (*sal ammoniac*) in **soldering** depends on the dissociation of the salt, by the heat of the iron, and the action of the liberated hydrogen chloride on the oxide which covers the surface of the metal to be soldered.

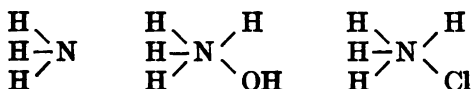
Some ammonium salts, like the nitrite (p. 514), when heated, give no ammonia (see also nitrous oxide and ammonium dichromate). Conversely, substances containing proteins (*e.g.*, gelatin), when heated, do give ammonia. Hence, liberation of ammonia is not proof that a substance is a salt of ammonium.

The test for ammonium salts is to warm them, dry or in solution, with a base, when the odor of ammonia becomes noticeable:



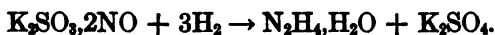
When the solution is used, it is the tendency of the  $\text{NH}_4^+$  and  $\text{OH}^-$  to unite to form the slightly ionized, molecular hydroxide that sets the other equilibria in motion. The principle at the basis of the change is thus the same as in neutralization (p. 398).

In ammonia, nitrogen is trivalent, while in the salts it appears to be quivalent:

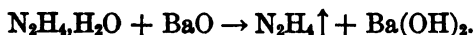


#### HYDRAZINE, HYDRAZOIC ACID, HYDROXYLAMINE

**Hydrazine  $\text{N}_2\text{H}_4$ .** — By reduction of a compound of nitric oxide and potassium sulphite by means of sodium amalgam,\* a solution of hydrazine hydrate is obtained:



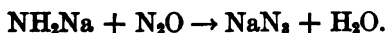
The same substance is more easily made from certain organic derivatives. When the hydrate is distilled with barium oxide, under reduced pressure, hydrazine is liberated:



Hydrazine is a white solid, which fumes in moist air, giving the hydrate once more. It melts at  $1.4^\circ$  and boils at  $113.5^\circ$ .

Hydrazine hydrate  $\text{N}_2\text{H}_5\text{OH}$  freezes at about  $-40^\circ$ , boils at  $118.5^\circ$ , and can be distilled without decomposition. Its aqueous solution is alkaline, and salts are formed by neutralization.

**Hydrazoic Acid  $\text{HN}_3$ .** — When nitrous oxide (*q.v.*) is led over sodamide at  $200^\circ$ , water is liberated and sodium hydrazoate remains behind:

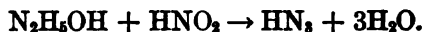


A dilute solution of the free acid is best obtained by distilling the lead

\* The sodium dissolved in the mercury interacts with the water, giving hydrogen (see Active state of hydrogen, below).

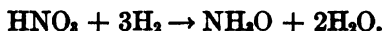


salt with dilute sulphuric acid. A similar solution may be made more directly by adding cold nitrous acid (*q.v.*) to a cold aqueous solution of hydrazine hydrate:



By repeated distillation of the solution the pure acid is obtainable. It boils at  $37^\circ$ . The operation is a dangerous one, as the pure acid is violently explosive, resolving itself into nitrogen and hydrogen with liberation of much heat:  $\text{HN}_3, \text{Aq} \rightarrow \text{H} + 3\text{N} + \text{Aq} + 61,600 \text{ cal.}$  The acid has an odor resembling hydrochloric acid, and the sodium salt has a taste like sodium chloride. The silver salt is insoluble in water. Thus the radical  $\text{N}_3$  confers properties similar to the radical  $\text{Cl}$ . The acid has a somewhat greater activity and degree of ionization than has acetic acid. Active metals, like magnesium, displace hydrogen from its solution. It neutralizes ammonium hydroxide and hydrazine hydrate, giving two salts,  $\text{NH}_4\text{N}_3$  and  $\text{N}_2\text{H}_5\text{N}_3$ . These constitute two additional compounds of nitrogen and hydrogen, but differ from ammonia and hydrazine in being ionogens. Lead hydrazoate  $\text{Pb}(\text{N}_3)_2$  is replacing mercury fulminate in the manufacture of percussion caps.

**Hydroxylamine  $\text{NH}_2\text{O}$ .**—Tin displaces hydrogen from dilute hydrochloric acid:  $\text{Sn} + 2\text{HCl} \rightarrow \text{SnCl}_2 + \text{H}_2$ , and this combination forms a reducing agent (see below). When dilute nitric acid (*q.v.*) is added to the mixture, a considerable part of it is reduced to hydroxylamine:



The hydroxylamine forms with water a weak base,  $\text{NH}_2\text{O.OH}$ , which interacts with the excess of acid, giving hydroxylamine hydrochloride  $\text{NH}_2\text{OCl}$ . By more complete reduction of part of the nitric acid, some ammonium chloride  $\text{NH}_4\text{Cl}$  is formed at the same time. To secure the salt of hydroxylamine, the tin ions are removed by means of hydrogen sulphide, which precipitates stannous sulphide. The filtered solution is then evaporated to dryness, the hydroxylamine hydrochloride is extracted from the residue with absolute alcohol, and this alcoholic solution is finally evaporated in turn. The hydrochloride is a white crystalline salt.

A better yield (80 per cent) is obtained by placing 50 per cent sulphuric acid (or 25 per cent  $\text{HCl}$ ) in an electrolytic cell. The negative electrode is a pool of mercury, or a small piece of lead

amalgamated with mercury. Hydrogen is liberated on the surface of the mercury, which acts as a contact agent, and nitric acid is allowed to flow very slowly from a tube on to the surface of the mercury. The cell is kept cool, and a high current density, by using a small mercury surface, is required for a good yield. The equation is the same as that given above.

Anhydrous hydroxylamine is best obtained by heating the orthophosphate  $(\text{NH}_4\text{O})_2\text{PO}_4$  under reduced pressure:



It is a white solid melting at  $33^\circ$  and boiling at  $58^\circ$  at 22 mm. pressure. Even before melting (above  $15^\circ$ ), it begins to decompose, and explodes at or below  $130^\circ$ . In chemical behavior it is like ammonia. With water it forms a base which combines with acids, but is less active than ammonium hydroxide. It is a stronger reducing agent than ammonia, precipitating silver from a solution of silver nitrate.

The union with acids indicates that the molecule of hydroxylamine is unsaturated, and hence the nitrogen unit is supposed to be trivalent:



**Halogen Compounds of Nitrogen.**—When ammonium chloride solution is treated with excess of chlorine, drops of an oily liquid, **nitrogen trichloride**  $\text{NCl}_3$ , are formed:



It is extremely explosive, resolving itself into its constituents with liberation of much heat.

When a solution of iodine in potassium iodide solution (p. 276) is added to aqueous ammonia, a brown precipitate is formed. The composition of the substance depends upon the temperature. Thus, at  $-60^\circ$  it is  $\text{NI}_3 \cdot 12\text{NH}_3$ , at  $-40^\circ$   $\text{NI}_3 \cdot 3\text{NH}_3$ , at  $-35^\circ$   $\text{NI}_3 \cdot 2\text{NH}_3$ , and at  $-25^\circ$  and above  $\text{NI}_3 \cdot \text{NH}_3$ . The first three, when the temperature rises, lose ammonia, but the last, commonly named **nitrogen iodide**, explodes. It may be handled while wet, but when dry decomposes into its constituents with violent explosion if touched with a feather. The ammonia it contains is like that in  $\text{CaCl}_2 \cdot 8\text{NH}_3$  (p. 517), and resembles water of hydration.

**Exercises.** — 1. When moist air is used as a source of nitrogen, what advantage is there in using copper rather than the less expensive metal iron, for removing the oxygen (p. 514)?

2. How many grams of water at  $0^{\circ}$  could be frozen (p. 144) by the removal of the heat required to evaporate 50 g. of liquid ammonia (p. 517)?

3. How many grams of ammonia are contained in 1 l. of "concentrated ammonia" (p. 517)? What would be the change in volume, if this were made by mixing liquid ammonia with water?

4. What are the ions of hydrazine hydrate (p. 521)? Formulate (p. 387) the neutralization of this base with sulphuric acid.

5. What is the object attained by distilling under reduced pressure in making hydrazine (p. 521) and hydroxylamine (p. 522)?

6. Classify (p. 228) the interaction of a nitride with water (p. 514), and of chlorine-water and ammonium chloride (p. 523), and the results of heating ammonium nitrite (p. 514) and ammonium chloride (p. 520).

7. What substances are present in ammonium hydroxide solution? When the liquid is heated, what happens to each? Formulate the system.

## CHAPTER XXVI

### OXIDES AND OXYGEN ACIDS OF NITROGEN

THE names and formulæ of the oxides and oxygen acids of nitrogen are as follows:

Nitrous oxide $N_2O$	$\longleftarrow$	Hyponitrous acid $H_2N_2O_2$
Nitric oxide $NO$		
Nitrous anhydride $N_2O_3$	$\longleftrightarrow$	Nitrous acid $HNO_2$
Nitrogen tetroxide $N_2O_4$ and $NO_2$		
Nitric anhydride $N_2O_5$	$\longleftrightarrow$	Nitric acid $HNO_3$

All the oxides are endothermal compounds, yet, with the exceptions of the third and the last, they are all relatively stable. The acids, when deprived of the elements of water, yield the oxides opposite which they stand. Conversely, excepting in the case of nitrous oxide, the anhydrides with water give the acids. All of these substances are obtained directly or indirectly from nitric acid — nitric anhydride by removal of water, the others by reduction. We turn, therefore, first, to nitric acid, its sources and properties.

#### NITRIC ACID

**Sources.** — Sodium nitrate, or Chile saltpeter (*caliche*), is found in a desert region near the boundary of Chile and Peru, and chiefly in the former country. The deposit is about 5 feet thick, 2 miles wide, 220 miles in length, and contains 20 to 60 per cent of the salt. Purification is effected by recrystallization. Potassium nitrate, or Bengal saltpeter, is found in the soil in the neighborhood of cities in India, Persia, and other oriental countries. It arises from the oxidation of animal refuse (*cf.* p. 517) through the mediation of nitrifying bacteria. The potash and lime in the soil, along with the product of oxidation of the nitrogen, give nitrates of potassium and calcium. The aqueous extract of this soil is treated with wood ashes, which contain potash  $K_2CO_3$ . It is poured off from the calcium carbonate thus precipitated, and is finally evaporated. The organic compounds of nitrogen originally contained in guano, a valuable fertilizer, are frequently found to have been changed into nitrates by nitrifying bacteria.

The action of the nitrifying bacteria may be imitated in a rough way [Lect. exp.]. Air is caused to pass slowly through concentrated aqueous ammonia, whereby it becomes mixed with ammonia gas. This mixture is led through a wide tube containing platinized asbestos and is then discharged into a large flask. When the asbestos is warmed, it begins to glow, and thereafter the action maintains itself. A part of the ammonia is oxidized to nitric acid, which combines with the excess of ammonia, giving ammonium nitrate. This salt forms a cloud of solid particles which settle in the flask. This process is used on a commercial scale.

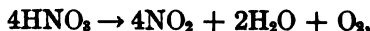
**Manufacture.**—When any nitrate is treated with any acid, nitric acid is formed by a reversible double decomposition. As sodium nitrate is the cheapest salt of nitric acid, it is always employed. For the same reason, and on account of its activity and, above all, because of its relative involatility, sulphuric acid is used to displace it:



The nitric acid is rather volatile (b.-p.  $86^\circ$ ), while sulphuric acid (b.-p.  $330^\circ$ ) is much less so, and the two salts are not volatile at all. Thus the interaction proceeds to completion very easily (*cf.* p. 207, see also p. 559). The materials are heated in cast-iron stills, and the vapor is condensed in glass or earthenware pipes surrounded by water. In many factories a reduced pressure is maintained in the stills and condensers, in order that the distillation may take place at the lowest possible temperature. This precaution is taken to reduce to a minimum the partial decomposition of the nitric acid (see below).

**Physical Properties.**—Nitric acid is a colorless, mobile liquid (density 1.52) boiling at  $86^\circ$ , and freezing to a solid (m.-p.  $-47^\circ$ ). It fumes strongly when its vapor issues into moist air (*cf.* p. 211). An aqueous solution containing 68 per cent of the acid boils at  $120.5^\circ$ , while the pure acid, pure water, and all other mixtures, boil at lower temperatures, and have, therefore, higher vapor pressures. On this account a more dilute acid, when heated, loses water until it reaches this strength. The 68 per cent nitric acid of constant boiling-point (p. 211) forms the "concentrated nitric acid" of commerce (density 1.41).

**Chemical Properties.**—1. Like chloric acid (p. 482), and other oxygen acids of the halogens, nitric acid is most stable when mixed with water. The pure (100 per cent) acid decomposes while being distilled:



yet not with explosive violence like chloric acid. The distillate is colored brown by dissolved nitrogen tetroxide  $\text{NO}_2$ . Repeated distillation finally leaves 68 per cent of the acid, mixed with 32 per cent of water formed by the above decomposition. The acid of constant boiling-point is, therefore, reached, as usual, from more concentrated as well as from less concentrated specimens.

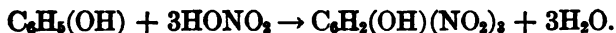
"Fuming" nitric acid is brown in color, and contains a considerable amount of dissolved nitrogen tetroxide. It is made by distilling the acid with a little starch. The latter reduces a part of the nitric acid and liberates more of the tetroxide than does mere distillation.

2. Nitric acid, when dissolved in water, is highly ionized, and is therefore **active** as an **acid**. By interaction with hydroxides and oxides it forms nitrates.

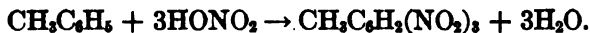
3. When pure nitric acid (b.-p.  $86^\circ$ ) is poured upon phosphoric anhydride, the latter combines with the elements of water, and distillation gives **nitric anhydride**:  $2\text{HNO}_3 + \text{P}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_5 \uparrow + 2\text{HPO}_3$ . The **anhydride** is a white solid melting at  $30^\circ$  and boiling at  $45^\circ$ . It unites vigorously with water to form nitric acid. It cannot be kept, as it decomposes into nitrogen tetroxide and oxygen,  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ , with liberation of heat.

4. Like the unstable oxygen acids of the halogens, nitric acid is an **oxidizing agent** even when diluted with water. The multiplicity of the products into which it may be decomposed by reduction, however, renders separate treatment of this property necessary (see p. 534).

5. Nitric acid interacts energetically with many compounds of carbon to give **nitro-derivatives**. Thus, when heated with phenol  $\text{C}_6\text{H}_5\text{OH}$  (carbolic acid) it gives **picric acid** (trinitrophenol)  $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ , which crystallizes in yellow needles in the mixture. This is a yellow dye, used also as an explosive (lyddite):



The presence of water decreases the activity of the molecules. Hence, in this sort of action, which is not ionic, not only is concentrated nitric acid employed, but concentrated sulphuric acid is added to assist in the elimination of the water (cf. p. 438). Nitric acid, heated with toluene  $\text{C}_6\text{H}_5\text{CH}_3$ , gives **trinitrotoluene**:



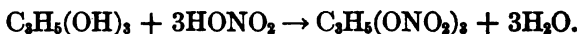
This substance (T.N.T.) is used for filling "high explosive" shells, because it can be melted (m.-p.  $81.5^\circ$ ) and poured in, making the

filling easy, safe, rapid, and complete. It is not easily exploded by shocks during transportation, but it explodes instantaneously and completely with a detonator. The following equation shows, roughly, the decomposition, and the large amount of carbon set free explains the black smoke produced:

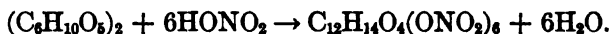


It will be seen that the group  $\text{NO}_2$  has taken the place of hydrogen, which was formerly attached directly to the carbon of the phenol or toluene. Compounds of this kind are called nitro-derivatives.

6. Organic compounds of another class, the alcohols (*q.v.*), interact with molecular nitric acid in a different way. The latter is mixed with sulphuric acid with the same object as before. Thus, when glycerin is added slowly to the cooled mixture, glyceryl nitrate (so-called **nitro-glycerine**, see below) is produced:

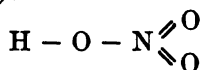


Here it is the hydrogen of the hydroxyl groups that is displaced by  $\text{NO}_2$ . The action is not ionic, and the product is not an ionogen. **Gun-cotton** is made by this action, cotton (cellulose) being employed:



7. Nitric acid produces substances of bright-yellow color, known as **xanthoproteic acids**, when it comes in contact with proteins, *e.g.*, in the skin, or in wool. Hence nitric acid stains woollen clothing yellow. This reaction is used as a test for proteins.

The chemical properties of nitric acid are best represented by the graphic formula (see p. 540):



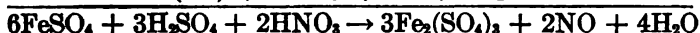
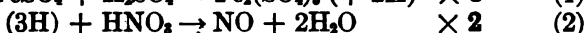
8. **Nitron** (1,4-diphenyl-endanilino-dihydrotriazole)  $\text{C}_{20}\text{H}_{12}\text{N}_4$  gives a fairly insoluble nitrate  $\text{C}_{20}\text{H}_{12}\text{N}_4\text{HNO}_3$ , when nitron acetate is added to a solution containing nitric acid. Nitric acid can be determined quantitatively by weighing the precipitate.

**Nitrates.** — The nitrates of the metallic elements are all more or less easily soluble in water. When heated they decompose in one or other of three ways (see pp. 531, 537, 539). Sodium nitrate is used largely as a fertilizer. Much is employed in sulphuric acid manufacture, and the rest for conversion into potassium nitrate and

in making nitric acid. Potassium nitrate is used, along with sulphur and charcoal, in the manufacture of gunpowder. The individual nitrates are described under the metallic elements they contain.

### NITRIC OXIDE AND NITROGEN TETROXIDE

**Preparation of Nitric Oxide NO.** — Pure nitric oxide is obtained by adding nitric acid to a boiling solution of ferrous sulphate in dilute sulphuric acid, or of ferrous chloride in hydrochloric acid:



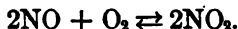
The first partial equation does not take place at all unless an oxidizing agent like nitric acid is present (p. 320). The multiplication of the two partial equations by 3 and 2, respectively, is required in order that the hydrogen, which is not a product, may cancel out. This action is used as a means of determining the quantity of nitric acid in a solution, or of nitrates in a mixture, by measurement of the volume of nitric oxide evolved.

Nitric oxide may also be obtained when sufficiently dilute nitric acid (density 1.2) acts upon copper (see p. 535). Although some nitrous oxide and nitrogen are formed, this interaction furnishes a more convenient method of generating the gas in the laboratory (see also p. 532).

**Properties of Nitric Oxide.** — Nitric oxide is a colorless gas. In solid form it melts at  $-167^\circ$  and the liquid boils at  $-153.6^\circ$ . Its solubility in water is slight. The density of the gas shows the formula to be NO; and there is *no* tendency to form a polymer, such as  $\text{N}_2\text{O}_2$ , even at low temperatures.

Nitric oxide is the most stable of the oxides of nitrogen. Vigorously burning phosphorus continues to burn in the gas, the heat evolved liberating the oxygen required for the continuation of the combustion. Burning sulphur and an ignited taper, however, cannot decompose the gas, and are extinguished.

Nitric oxide has two characteristic properties. It unites directly with oxygen in the cold to form the reddish-brown nitrogen tetroxide:



This can be used as a test for even a trace of free oxygen, mixed with



other gases. The same result follows when it is led into warm concentrated nitric acid:  $\text{NO} + 2\text{HNO}_3 \rightleftharpoons 3\text{NO}_2 + \text{H}_2\text{O}$ .



FIG. 122.

It also unites with a number of salts, the compound in the case of ferrous sulphate,  $\text{FeNO} \cdot \text{SO}_4$  (a molecular compound, see below), being capable of existence in solution and possessing a brown color. The NO is part of the positive ion  $\text{FeNO}^{++}$ , and migrates with it (Manchot).

Since ferrous sulphate will first reduce nitric acid to nitric oxide (p. 529), and the excess of the salt will then give a brown color with the product, a delicate test for nitric acid is founded upon the above action. The substance supposed to contain a nitrate is mixed with a strong solution of ferrous sulphate, and concentrated sulphuric acid is poured down the side of the tube so as to lie below the lighter mixture (Fig. 122). At the surface of contact the sulphuric acid liberates the nitric acid, this is reduced to nitric oxide, the molecular compound is formed, and a brown layer is seen. Even when the amount of the nitrate is very small, the brown tint is distinctly visible, by contrast with the colorless liquids above and below it.

**Molecular Compounds.**—When substances formed by union of two compounds have a prevailing tendency to decompose into the same two materials, and exhibit the chemical properties of their constituents rather than individual ones of their own, they are often called **molecular compounds**. Thus the above substance  $\text{FeNO} \cdot \text{SO}_4$  gives off the nitric oxide again when warmed. Similarly, hydrates (pp. 150–154) are formed by union of salts or other substances with water, and are, for the most part, decomposed by solution. Double salts (p. 402), such as ferrous-ammonium sulphate  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , of which very many are known, are of the same character. They are stable only in the solid form. There are also compounds of salts with ammonia (see Copper and silver), and with carbon monoxide CO, one such compound being formed with cuprous chloride (*q.v.*).

The name *molecular compounds* is derived from the supposition that, in these compounds, the molecules of the components retain their integrity to some extent and are thus ready to be liberated. This is an attempt to explain the fact that the behavior is that of the constituents. It distinguishes molecular compounds from substances

like ammonium chloride and phosphorus pentachloride. The former may be made by union of HCl and  $\text{NH}_3$ , but usually behaves rather as if composed of  $\text{NH}_4$  and Cl. The latter (*q.v.*) dissociates into  $\text{PCl}_3$  and  $\text{Cl}_2$ , but with water gives phosphoric acid (*cf.* p. 210), which is derivable from the pentachloride only. The distinction is of practical rather than theoretical importance, however, for there are all gradations in the behavior of molecular compounds. It is useful simply as a rough means of classifying and remembering certain facts.

Distinguishing molecular compounds from ordinary compounds is further justified by the fact that the constituents of molecular compounds often seem to be saturated (p. 427), and no ordinary valences are available for holding the new material. Thus in  $\text{Ca}^{++}\text{Cl}_2^-$  the ordinary valences are all saturated. Yet the salt forms the hydrate  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  with water  $\text{H}_2^+\text{O}^{--}$ , which is likewise a saturated compound. The conception of molecular compounds implies, therefore, the idea of a sort of *valence of molecules*. Thus  $\text{FeSO}_4$  forms  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , and  $\text{FeSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , in all of which *seven* other molecules are combined with it. The sulphates of other bivalent metals (*q.v.*), such as copper and magnesium, form molecular compounds of the same nature. Ammonium chloride, on the other hand, is not a molecular compound, because, although  $\text{NH}_3$  unites with HCl, HBr, HI, and HF, yet nitrogen is quinquivalent, and substances like  $\text{N}_2\text{O}_5$ ,  $\text{NH}_4\text{Cl}$ , etc., may fitly be regarded as ordinary compounds.

**Preparation of Nitrogen Tetroxide  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$ .**—This substance is liberated by heating nitrates, other than those of potassium, sodium, or ammonium, such as the nitrates of lead and copper:

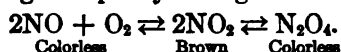


The nitrates of metals above mercury in the E. M. series (p. 404) leave the oxide. The nitrates of mercury and of the metals below it leave the metal. When the mixed gases are led through a U-tube immersed in a freezing mixture, the tetroxide condenses as a pale-yellow liquid (b.-p.  $22^\circ$ , m.-p.  $-10.5^\circ$ ), and the oxygen passes on.

The compound may also be made by direct union of nitric oxide and oxygen, or by oxidation of nitric oxide by concentrated nitric acid (p. 530). It is likewise almost the sole product of the interaction of *concentrated* nitric acid and copper (see p. 535). If any nitric oxide were produced by the primary action, it would be oxidized to nitrogen tetroxide in passing up through the concentrated acid.

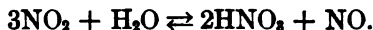
**Properties of Nitrogen Tetroxide.** — The most striking peculiarity of this gas is that, when hot, it is deep brown in color, and when cold, pale yellow. The density of the gas decreases very rapidly from 22° to 140°, and increases again as the temperature falls. The molecular weights calculated from these observations are: at 22°, 90; at 70°, 55.6; at 135°, 46.3; at 154°, 45.7. Now the molecular weights corresponding to the formulæ  $N_2O_4$  and  $NO_2$  are 92 and 46, respectively, so that these results mean that the deep-brown gas is  $NO_2$ , and that as this is cooled it combines to form the colorless  $N_2O_4$ . Measurement of the depression the substance causes in the freezing-point (cf. p. 336) of glacial acetic acid gives the molecular weight 92, so that in solution and at the temperature of freezing acetic acid (below 17°) the substance is all  $N_2O_4$ .

When the temperature is carried above 154°, by passing the brown gas through a red-hot tube, the brown color disappears once more, and nitric oxide and oxygen are formed. On cooling, the same steps through brown gas to pale-yellow gas are retraced:



Since nitrogen tetroxide yields free oxygen more readily than does nitric oxide, phosphorus burns readily in it; a taper, or burning sulphur, however, is extinguished. It has powerful oxidizing properties, and "fuming nitric acid," which contains it in solution, is employed when oxidation is the special object in view. For the same reason, the gas is sometimes used in bleaching flour.

This oxide is intermediate in composition between nitrous and nitric anhydrides, and, when dissolved in cold water, gives both nitric and nitrous acids:  $N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$ . If a base is present, a mixture of the nitrate and nitrite of the metal is produced (cf. p. 474). When the water is not cooled, the nitrous acid (*q.v.*), being unstable, gives nitric oxide and nitric acid, so that the result is:



#### NITRIC ACID FROM ATMOSPHERIC NITROGEN

**The Reactions Involved.** — Nitrogen and oxygen have no tendency to unite at room temperature to form nitric oxide. The union is endothermal, and is therefore favored by a high temperature (van't Hoff's law, p. 305):

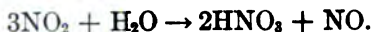


Even at 1922°, however, using atmospheric air, only 1 per cent

nitric oxide is formed, and at  $2927^{\circ}$ , 5 per cent. The electric discharge actually used gives about 1 per cent.

The mixture is next *cooled*, to permit the union of  $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$ , because (p. 532) nitrogen tetroxide is decomposed at about  $154^{\circ}$ , and therefore cannot be formed at  $1900^{\circ}$ .

Next, the air containing  $\text{NO}_2$  is passed through absorbing towers, down which *water* trickles, and nitric acid is formed:



The  $\text{NO}$  liberated combines with more atmospheric oxygen to form  $\text{NO}_2$ , which interacts again with the water, and practically no nitric oxide is lost.

Finally, the nitric acid is poured upon limestone  $\text{CaCO}_3$ , and the calcium nitrate formed is sold, for use as a fertilizer, under the name *air saltpeter*.

**The Plant used in the Fixation.** — At Notodden and elsewhere in Norway, the **Birkeland-Eyde** process (Fig. 123) is used. Hydro-

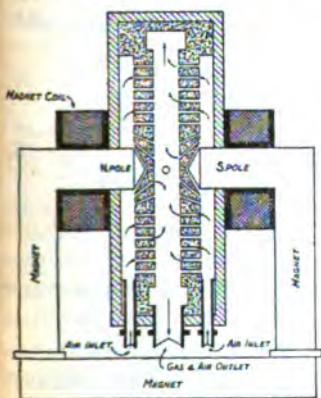


FIG. 123.

electric power is employed, and an arc discharge between two rods of carbon is spread, by the influence of large and powerful electromagnets, into a circular brush discharge several feet in diameter. The figure is a cross section of the space filled by the discharge, the small circle in the center

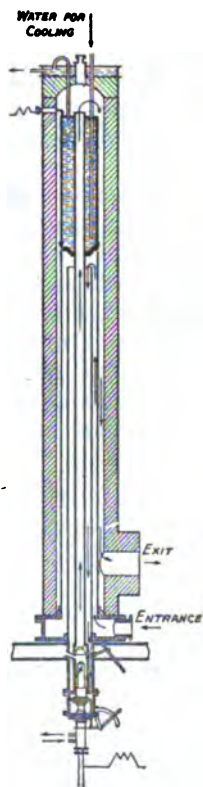


FIG. 124.

being a section of one carbon rod. Air is blown through the flame in such a way that none can avoid passing through at least a part of the heated area. The yield is about 70 g. of nitric acid per kilowatt-hour, and the net earnings are \$350,000 (1911).

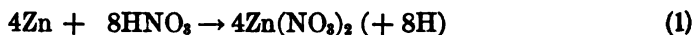
The **Badische process**, used in the same factories in Norway, employs a discharge through a tube over 20 feet long (Fig. 124). The stream of air rotates as it traverses the tube, so that every part is exposed to the discharge. The **Pauling process**, used at Gelsenkirchen in Germany and Nitrolee, South Carolina, uses preheated air and a different arrangement of the discharge.

Other reactions involving the fixation of atmospheric nitrogen are discussed under cyanamide (*q.v.*) and root nodules (p. 515).

#### OXIDIZING ACTIONS OF NITRIC ACID

When nitric acid gives up oxygen to any body, it is itself reduced. Hence, according to convenience, we shall refer to oxidations by, or reductions of nitric acid.

**Oxidation of Hydrogen.** — The metals preceding hydrogen in the electromotive series (p. 404) displace hydrogen from nitric acid, as they do from other acids. With metals more active than zinc, such as magnesium, a great part of the hydrogen escapes in the free condition. But, in the case of zinc and the metals below it, most or all of the hydrogen is oxidized to water by the nitric acid, and part of the acid is reduced (see Active hydrogen, p. 543). Thus, with zinc and *very dilute* nitric acid, almost the only product, aside from zinc nitrate, is ammonia:

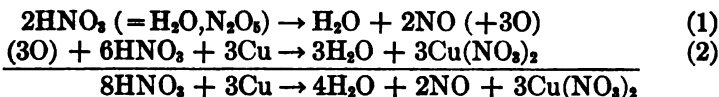


With the excess of nitric acid, ammonium nitrate is formed.

**Heavy Metals.** — The less active metals, such as copper and silver, do not displace hydrogen from dilute acids (p. 129), but reduce nitric acid, nevertheless, and are converted into nitrates. Platinum and gold (*cf.* p. 439) alone are not attacked. Thus, copper, with somewhat *diluted* nitric acid (density 1.2) gives cupric nitrate and nitric oxide NO.

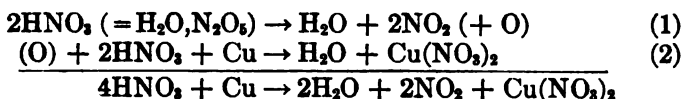
In making the equation for this action we may use the **anhydride plan** (p. 496), which is applicable whenever an oxygen acid gives an oxide by reduction. We resolve the formula of nitric acid into those of water and the **anhydride**  $\text{H}_2\text{O}, \text{N}_2\text{O}_5$  ( $= 2\text{HNO}_3$ ). This

shows that the two molecules of the acid will give 2NO, and 3O will remain:

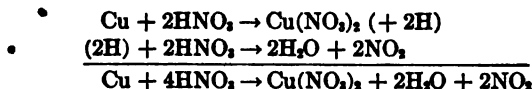


The nitric oxide is liberated as a colorless gas, but forms the brown tetroxide at once on meeting the oxygen of the air (p. 529).

When *concentrated* nitric acid is used with copper, almost pure nitrogen tetroxide is obtained:



The equations for actions like the above may be built up from partial equations of various kinds (cf. p. 269). Thus we may begin by forming the nitrate of the metal, and then use the balance, consisting of hydrogen, along with other molecules of nitric acid to secure the oxide and water:



As the subdivision is purely arithmetical (p. 270), this procedure does not involve the assumption that copper does actually displace hydrogen as a free element. Yet it would not necessarily be incorrect to make even this supposition. Although unable to liberate hydrogen in quantity from a dilute acid, copper must be held to displace a minute amount of it:



and to be restrained by the much more vigorous reverse action (p. 404) from continuing this operation. In this point of view the oxidation of the trace of free hydrogen by the excess of nitric acid continuously annihilates the possibility of reverse action.

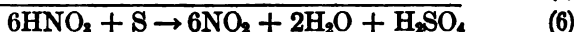
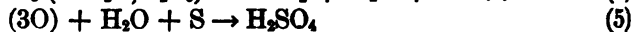
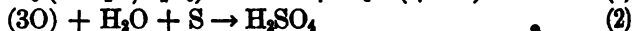
**Complexities of Oxidation by Nitric Acid.** — The above are types of the interactions of metals with nitric acid. In actual experiments the behavior is usually more complex. Thus, as a rule, the action is very slow at first, and gathers speed with the accumulation of the reduction products, which act catalytically.

Again, different concentrations of nitric acid give different products with the same metal. The reader should note the constant production of **nitric oxide with diluted acid**, and the invariable

formation of **nitrogen tetroxide with concentrated acid**. This is explained by the fact that nitrogen tetroxide cannot pass unchanged through a liquid containing much water, for it gives nitric acid and nitric oxide with the latter (p. 532). Conversely, where the nitric acid is concentrated, nitric oxide, even if formed by the interaction with the metal, must be oxidized to nitrogen tetroxide as it passes up through the liquid (p. 530). Note, also, that the nitrate of the metal is formed, if the nitrate is stable, *not* the oxide.

Finally, intermediate concentrations give mixtures of these two oxides, and, with zinc, even nitrous oxide  $N_2O$  and nitrogen may be found in considerable quantities in the gases evolved.

**Oxidation of Non-Metals.** — With non-metals the actions are different, in so far that these elements form no nitrates. Thus, sulphur boiled in nitric acid gives sulphuric acid, along with nitric oxide, equation (3), or with nitrogen tetroxide, equation (6), or with both, according to the concentration of the acid (see above):

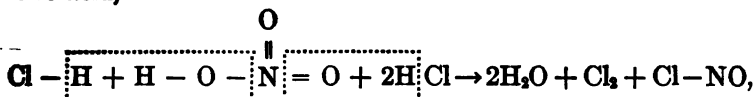


The reader will note (*cf.* p. 483) that a separate equation, (3) and (6), must be made for the formation of *each* reduction product. If  $NO$  and  $NO_2$  are both formed, they cannot arise from the same molecule of nitric acid. They result from two actions which are independent, although proceeding concurrently in the same vessel (*cf.* p. 483). Thus the equation:  $2HNO_3 + C \rightarrow H_2O + CO_2 + NO + NO_2$ , is a misrepresentation. It implies that equimolar quantities of the two oxides of nitrogen are formed. But this could occur only by chance, and the balance would be destroyed the next moment by the lowering in the concentration of the acid, giving the advantage to the nitric oxide.

**Oxidation of Compounds: Aqua Regia.** — Compounds like hydrogen sulphide, hydrogen iodide, and sulphurous acid, which are easily oxidized, interact with nitric acid. With diluted nitric

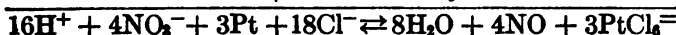
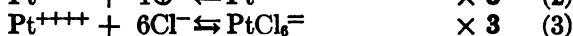
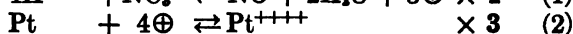
acid the products are free sulphur, iodine, and sulphuric acid, respectively.

The mixture of nitric acid and hydrochloric acid is known as *aqua regia*. Chlorine is set free by the oxidation of the hydrochloric acid,



and nitrosyl chloride NOCl is also formed. The liquid thus contains several oxidizing agents, nitric acid, hypochlorous acid (from  $\text{Cl}_2 + \text{H}_2\text{O}$ ), and some nitrous acid. It is frequently used in analysis, for example to oxidize sulphur (say, in cast iron or in minerals), the sulphuric acid formed being estimated by precipitation and weighing of barium sulphate (p. 440).

*Aqua regia* (Lat., *royal water*) received its name because it converted the "noble" metals, gold and platinum, into soluble compounds. This it does because the free chlorine, in presence of hydrochloric acid combines to form the exceedingly stable complex ions (*q.v.*)  $\text{AuCl}_4^-$  (see chlorauric acid  $\text{HAuCl}_4$ ) and  $\text{PtCl}_6^-$ , the negative ion of chloroplatinic acid:  $2\text{HCl} + 2\text{Cl}_2 + \text{Pt} \rightarrow \text{H}_2\text{PtCl}_6$ . Since the chloride-ion, rather than the free chlorine, is concerned, the following equations show the action more exactly:



Mercuric sulphide  $\text{HgS}$  is attacked because mercuric chloride is a very slightly ionized substance, particularly in presence of hydrochloric acid, with which it combines.

The idea that a nascent form of chlorine exists here is even more superfluous than is the similar assumption about oxygen.

#### NITROUS ACID, HYPONITROUS ACID, AND THEIR ANHYDRIDES

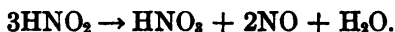
**Nitrites and Nitrous Acid.** — When the nitrates of potassium and sodium are heated, they lose one unit of oxygen, and the nitrites remain:





Commonly lead is stirred with the melted nitrate and assists in the removal of the oxygen. The litharge PbO which is formed remains as a residue when the sodium nitrite is dissolved for recrystallization.

When an acid is added to a *dilute* solution of a nitrite, a pale-blue solution containing **nitrous acid**  $\text{HNO}_2$  is obtained. The acid is very unstable, however, and, when the solution is warmed, it decomposes:



When a *concentrated* solution of sodium nitrite is acidified, the nitrous acid decomposes at once, and a brown gas containing the anhydride escapes:

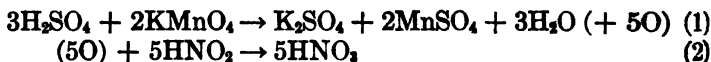


This behavior distinguishes a nitrite from a nitrate.

Reducing agents deprive nitrous acid of part or all of its oxygen:



Indigo is also converted by it into isatin (*cf.* p. 476). On the other hand, oxidizing agents which are sufficiently active, like acidified potassium permanganate, convert nitrous acid into nitric acid:



Nitrous acid is much used in the making of organic dyes.

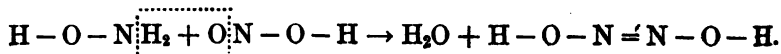
**Nitrous Anhydride  $\text{N}_2\text{O}_3$ .** — A study of the density of the gas arising from the decomposition of nitrous acid shows that, in the gaseous state, the anhydride is almost entirely dissociated:



When the mixture is led through a U-tube immersed in a freezing mixture at  $-21^\circ$ , a deep-blue liquid is obtained which appears to be the anhydride itself. This begins to dissociate before reaching its boiling-point, and at  $+2^\circ$  gives off nitric oxide.

The same equimolar mixture of the two gases is obtained by the action of water on nitrosylsulphuric acid (p. 433).

**Hyponitrous Acid  $\text{H}_2\text{N}_2\text{O}_2$ .** — This acid is formed by the interaction of hydroxylamine and nitrous acid in aqueous solution:



With nitrate of silver, the yellow, insoluble silver hyponitrite  $\text{Ag}_2\text{N}_2\text{O}_2$  is precipitated. When this salt is shaken with an ethereal solution of hydrogen chloride, the acid is liberated, and the insoluble silver chloride may be separated by filtration. Finally, evaporation of the ethereal solution leaves hyponitrous acid as a white solid. It explodes when heated, and its solution in water is an exceedingly feeble acid. The warm aqueous solution decomposes slowly, giving nitrous oxide:



and this change is *not* capable of reversal.

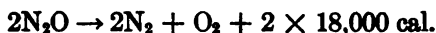
**Nitrous Oxide  $\text{N}_2\text{O}$ .** — Nitrous oxide is prepared by cautiously heating ammonium nitrate (the decomposition is exothermal), or a mixture of a salt of ammonium and a nitrate:



The steam condenses, and the nitrous oxide may be collected over warm water, or dried and compressed into steel cylinders.

Its solubility in cold water is considerable: at  $0^\circ$ , 130 volumes in 100; at  $25^\circ$ , 60 in 100. In dissolving, the gas forms no compound with water. The substance melts at  $-102.3^\circ$ , and boils at  $-89.8^\circ$ . The vapor tension of the liquid at  $0^\circ$  is 30.75 atmospheres; at  $12^\circ$ , 41.2 atmospheres; and at  $20^\circ$ , 49.4 atmospheres. The critical temperature is  $38.8^\circ$ .

A glowing splinter of wood bursts into flame in nitrous oxide, and phosphorus, sulphur, and other combustibles, burn in it with much the same vigor as in oxygen. In all cases oxides are formed, and nitrogen is set free. It does not interact with nitric oxide, however, as does oxygen (p. 529). The rapidity with which bodies combine with oxygen obtained from nitrous oxide is doubtless due to the fact that it is an endothermal compound, and the heat liberated by its decomposition assists the ensuing combustion:

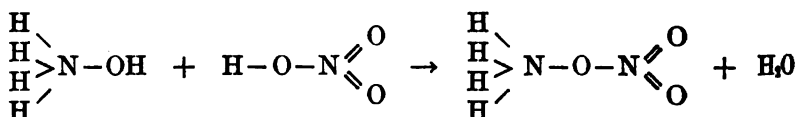


It is to be noted that the effect of the heat of decomposition will be partly offset by the dilution of the oxygen with nitrogen. Yet the proportion of nitrogen to oxygen is only half as great as in air, so that on the whole the conditions are much more favorable to combustion in this gas.

Nitrous oxide, when cold, does not behave like free oxygen. Metals do not rust in it, and the hæmoglobin of the blood is unable

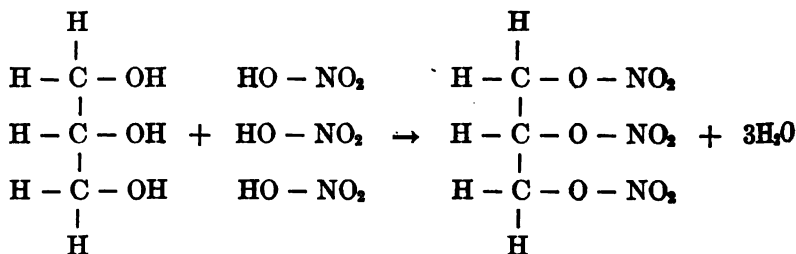
to use it as a source of oxygen. It was Davy who first observed that nitrous oxide could be taken into the lungs, and that, since it furnished no oxygen, insensibility followed its use. By suitable admixture of an amount of air sufficient to sustain life, it is employed as an anæsthetic for minor operations. The hysterical symptoms which accompany its use caused it to receive the name of "laughing gas."

**Graphic Formulæ of Nitric Acid and its Derivatives: Explosives.** — The following equation shows the graphic formulæ of nitric acid and of ammonium nitrate:



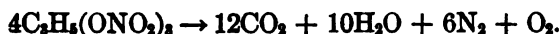
The structural formula of the latter is intended to explain the fact that the salt is able to exist at all, by representing the oxygen and hydrogen as being separated from one another and attached to different nitrogen units. When the equilibrium of the system is disturbed by heating, the oxygen and hydrogen unite to form water, an arrangement which is much more stable, and nitrous oxide (p. 539) escapes with the steam.

The behavior of nitroglycerine and guncotton (p. 528), as well as of ammonium nitrite (p. 514), is explained in the same way. These substances are made by actions which, like the above neutralization, take place in the cold, and the groups, containing the oxygen on the one hand and carbon and hydrogen on the other, become quietly united without more serious interaction. Thus the formation of nitroglycerine (p. 528) appears as follows:



When the nitroglycerine is heated, or receives a mechanical shock,

the oxygen all unites with the carbon and hydrogen, and the nitrogen escapes:



That nitroglycerine is a more sensitive explosive than gunpowder is due to the fact that, in the former, the materials required for the chemical change are already within the same molecule, whereas in the latter (*q.v.*) they are contained in the separate molecules of a mixture. Even after the most careful incorporation, the oxygen of the potassium nitrate can hardly be uniformly so near to the carbon, mechanically mixed with the salt, as are these elements in nitroglycerine or guncotton. In the latter the oxidation of the hydrogen and carbon is intramolecular.

Substances like hydrazoic acid (p. 521) and nitrogen iodide (p. 523) might seem to constitute a third kind of explosive. Here the change consists in the resolution of the compound into its constituents. Still, if we consider the case of hydrazoic acid, for example:  $2\text{N}_3\text{H} \rightarrow 3\text{N}_2 + \text{H}_2$ , we see that the action consists, after all, in the union of the constituents to form the more stable combinations  $\text{N}_2$  and  $\text{H}_2$ . It is, therefore, similar in principle to the explosion of nitroglycerine.

**Smokeless Powder and Dynamite.** — Dried guncotton (p. 528) simply burns briskly (deflagrates) when set on fire. Whether wet or dry, it explodes, but only from a suitable shock, such as that produced by fulminate of mercury  $\text{Hg}(\text{ONC})_2$ , used in percussion caps. In pure form it is used only in torpedoes or submarine mines. Like nitroglycerine (p. 541), it explodes too rapidly, and would burst the gun, or pulverize the ore or coal if used for blasting. Neither of these substances "explodes downwards only." The explosion strikes the air with equal violence, but the *effect* on the air escapes notice because it is not permanent, while the shattering of a rock or plate of steel remains.

**Cordite**, one variety of smokeless powder, is made by dissolving guncotton (65 parts), nitroglycerine (30 parts), and vaseline (5 parts) in acetone. The resulting paste is rolled out and cut into small pieces. When the acetone evaporates, the horny cordite remains. These explosives are *smokeless* because, unlike gunpowder and T.N.T., they yield no solids when they decompose (see equations).

Various forms of dynamite are made like cordite, excepting that sodium or ammonium nitrate and sawdust or flour are added, so

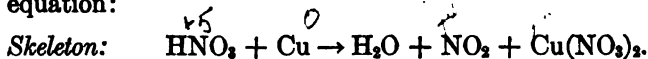
that the rate of explosion may be regulated and the coal or ore may be split up, but not shattered or pulverized.

**Plastics.** — A guncotton, less completely "nitrated" by nitric acid, when worked between rollers with camphor and a little alcohol gives a viscous solution (Parkes, before 1855). When the alcohol evaporates, transparent, colorless celluloid (first made by Hyatt) remains. The moist dough is rolled into sheets to make photographic films. By adding dyes and "fillers," and molding the dough, black combs, brush handles, white knife handles, etc., can be manufactured.

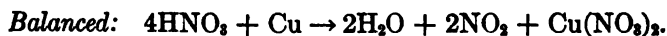
**Collodion** is a solution of the same guncotton in a mixture of alcohol and ether. When collodion is forced through minute holes in a steel dye, the threads dry as they come out and can be wound on spools. Treatment with an alkali "denitrates" the threads, restoring the composition to that of the original cotton. The product, one of the forms of **artificial silk**, is at least as brilliant as the real article (a protein, not related chemically to cotton), and susceptible of being dyed to any desired tint.

**Balancing Equations.** — The reader should practice the balancing of the equations for oxidations occurring in this chapter using all the methods. In the text, we have used the anhydride plan (p. 535) and that of partial equations (p. 538). To illustrate the other two plans, take, for example, the action of concentrated nitric acid on copper (p. 535).

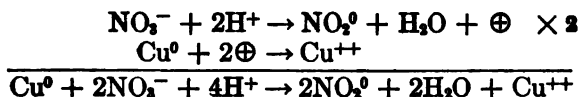
**Positive and negative valence method** (p. 493). Write the skeleton equation:



We perceive that on the left the valence of O is  $-6$  and of H  $+1$ ; that of N is therefore  $+5$ . That of Cu is zero. On the right the valence of N is  $+4$  and of Cu  $+2$ . Evidently,  $2\text{N}$  changing from  $2 \times +5$  to  $2 \times +4$  will furnish  $+2$  for the copper. We note also that  $2\text{NO}_2$  is required, without change, for  $\text{Cu}(\text{NO}_3)_2$ . Hence altogether  $4\text{HNO}_3$  is needed on the left, and gives  $2\text{NO}_2$ :



**Positive electrical charge plan** (p. 496). In the skeleton equation (above) we first separate the oxidizing ions and their products from the oxidized substance and the change it undergoes:



The first partial equation produces  $\oplus$ , while the second requires  $2\oplus$ , and hence the former is multiplied by 2 before the addition takes place. Since  $\text{NO}_3^-$  is the only acid radical present, it is understood that cupric nitrate is the salt formed.

**Active ("Nascent") Hydrogen.**—When hydrogen gas is led through cold nitric acid, little or no action occurs. But (p. 534) when zinc, which interacts with acids to give hydrogen, is placed in nitric acid the latter is reduced. To explain the apparently greater activity of the hydrogen in the second instance, we note the fact that it is liberated *on the surface of the zinc*. The contact (catalytic) effect of the zinc increases its activity. Many metals have, in a greater or less degree, this power of increasing the activity of hydrogen. Thus, hydrogen absorbed in platinum or palladium (p. 124), or liberated by electrolysis on poles made of these metals, reduces nitric acid readily. Other elements, such as the oxygen in making sulphur trioxide (p. 428), are also rendered more active by contact agents like platinum.

This **more active** state of hydrogen is described as the **nascent** state, because it happens to be a common condition of hydrogen when associated with substances which produce it. The active state has, however, no necessary connection with such an immediately preceding act of liberation, as the platinum and sulphur trioxide illustrations, and the following experiment [Lect. exp.] show: Three test-tubes are filled with very dilute potassium permanganate solution. Zinc dust, added to one, generates hydrogen and causes decolorization. A little platinum black is added to the second, and hydrogen gas is led through this and the third. The contact action of the platinum enables the hydrogen quickly to reduce the permanganate, while the third portion remains unaltered.

The term nascent hydrogen is used in different senses, in a very confusing way. (1) It may mean nascent, literally, that is, newly born or liberated. (2) It is used also to mean different-from-ordinary, or, in fact, an allotropic form of hydrogen. (3) It is often limited to mean one particular allotrope, namely, atomic hydrogen. (4) It is used by Haber and others, as we have used it above, to mean hydrogen activated by contact with a metal. (5) Finally, its activity is explained as being due to the larger amount of free energy contained in zinc plus

acid plus reducing agent, as compared with the free energy contained in free hydrogen plus reducing agent. The last is identical with the explanation of the activity of oxidizing agents (p. 479). The word nascent is, of course, a misnomer, excepting in connection with (1).

The following statements will enable us to determine which of these five conceptions are most in accord with experimental facts. This form of hydrogen has never been observed or isolated as a substance (against 1, 2, 3). If it is an allotropic form (2, 3), its degree of activity can be defined quantitatively. In point of fact, however, concentrated sulphuric acid gives, with copper, sulphur dioxide (p. 425), and with zinc, hydrogen sulphide (p. 119), so that the hydrogen (if it is the active agent) is much more active in the second case. Again, in electrolyzing a dilute acid, the dissolved atmospheric oxygen is reduced to hydrogen peroxide, provided the electrode is made of platinum (p. 317), but not if it is made of carbon. We saw also that hydrogen liberated by electrolysis on a surface of mercury gives a better yield of hydroxylamine (p. 522), than will any other metallic electrode. Yet the hydrogen must be the same in all cases (against 1, 2, 3; favors 4). Again, hydrochloric acid and some nitric acid, with zinc, give ammonia (p. 534), with magnesium no ammonia, with tin ammonia and hydroxylamine (p. 522). Here again the hydrogen is the same, but the metallic contact agent is different, and the free energy of the acid with each metal is different (against 1, 2, 3; favors 4 and 5). Some one found that nitrous oxide  $N_2O$  could be prepared by heating dry potassium nitrate with anhydrous formic acid  $HCO_2H$ :  $2KNO_3 + 6HCO_2H \rightarrow N_2O \uparrow + 4CO_2 + 5H_2O + 2KCO_2H$ . Formic acid, as a whole, has undoubted reducing power, so why drag in nascent hydrogen, as the discoverer did in this case? Finally, since hydrogen and chlorine do not unite in the cold, when sulphuric acid and common salt give hydrogen chloride, to be consistent we must suppose that nascent hydrogen and nascent chlorine were formed and combine. In other words, every union of two elements, other than direct union, must be explained by nascent action, although in double decomposition this logical necessity is uniformly overlooked.

There seems to be no question that contact with different metals confer on free hydrogen the ability to produce different chemical changes in the same substance. It is also clear that the extra energy with which hydrogen is delivered from some chemical actions, as compared with others, must appear to give it different degrees of activity.

**The Principle of Transformation by Steps.**—It may have occurred to the reader as strange that it should be possible to make nitric anhydride by distilling a warm mixture (p. 527) when the product decomposes spontaneously, even when kept in the cold. How can a compound be fitted together under certain conditions, when under the same or, even, under more favorable conditions it proves to be incapable of continued existence? We should expect rather that obtaining the products of its decomposition would have been the only result of the effort to make it.

Extraordinary as this fact appears to be, it is nevertheless very commonly encountered. Perchloric acid is made by a distillation (p. 484) and afterwards breaks up of its own accord. So, also, hypochlorites are formed first and can be isolated. But under the same conditions the further transformation to chlorates will occur (p. 480). A simple case is that of sulphur made by precipitation (p. 422) at the ordinary temperature. Although it is naturally solid below  $119^{\circ}$ , yet, when first thrown down, it is in the form of liquid droplets which, if undisturbed, may remain fluid for weeks. Similarly, sulphur vapor condenses on glass in drops which remain liquid for years, unless they are touched or rubbed. Finally, a supersaturated solution (p. 193) is not unlike cold liquid sulphur.

In all these cases there is a possibility of further change, which, when it comes, will liberate heat or some other form of energy. Thus, heat is set free when the liquid sulphur is precipitated. The amount of heat would have been greater, by the heat of fusion of the sulphur, if solidification had occurred simultaneously. But, in spite of the existence of this justification for the final step, this step is not taken. So, the decomposition of the vapor of the perchloric acid or of the nitric anhydride would have added to the amount of energy liberated as heat, but this additional step was postponed. In other words, **transformations which proceed spontaneously and with evolution of heat may go forward by steps, when there are intermediate substances, or allotropic forms, capable of existence.** This is known as the **principle of transformation by steps**, and was first formulated by Ostwald.

**Exercises.** — 1. Make the equation for the interaction of ferrous chloride, hydrochloric acid, and nitric acid (p. 529), and for all the actions concerned when the test for a nitrate (p. 530) is applied to sodium nitrate. What volume (at  $0^{\circ}$  and 760 mm.) of NO is obtained from one formula-weight of nitric acid (p. 265, Ex. 4)?

2. Should you classify as molecular compounds (p. 530): Chlorine hydrate, ammonium hydroxide,  $KI_3$  (p. 276), sulphurous acid, sodium tetrasulphide (p. 422)? Justify your answer.

3. At  $70^{\circ}$ , what proportions of the molecules of nitrogen tetroxide are in the forms of  $NO_2$  and  $N_2O_4$  respectively (p. 532)? At the same temperature what fraction of the material, by weight, is in the former condition? What are the relative volumes of the tetroxide, and of the nitric oxide and oxygen obtained by its decomposition (p. 532)?



4. Make an equation showing the production of nitrous oxide by the action of zinc on nitric acid.

5. Make the correct equations showing the formation of nitric oxide and nitrogen tetroxide by the interaction of carbon and nitric acid (p. 536).

6. Justify the graphic formula assigned to nitric acid (p. 540).

7. Using the anhydride method (p. 496), make the equations for the interactions of  $N_2O_4$  and water (p. 532) and of permanganic acid and nitrous acid (p. 538).

8. In the action of zinc on dilute nitric acid (p. 534), why is not the ammonia given off as a gas? How should you show that it was formed at all?

9. Make equations for the interaction of iron with diluted and with concentrated nitric acid, respectively (p. 535). The iron gives ferric nitrate  $Fe(NO_3)_3$ .

10. Give the three ways in which nitrates decompose when heated, with one equation illustrating each.

11. Make all the equations for oxidations on pp. 535 and 536, using the methods illustrated on p. 542.

## CHAPTER XXVII

### PHOSPHORUS

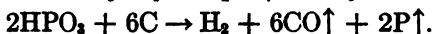
**The Chemical Relations of the Element.** — There are many things in the chemistry of phosphorus and its compounds which remind us of nitrogen. Yet these are largely referable to the fact that the elements are both non-metals and both have the same valences, viz., three and five. The behavior of the compounds is often very different. For the present it is sufficient to say that both give compounds with hydrogen,  $\text{NH}_3$  and  $\text{PH}_3$ , and both yield oxides of the forms  $\text{X}_2\text{O}_3$ ,  $\text{X}_2\text{O}_4$ , and  $\text{X}_2\text{O}_5$ . The first and last of these oxides are acid-forming, and phosphorus, therefore, gives acids corresponding to nitrous and nitric acids, although there is more variety in the proportion of water combined with the anhydride (*cf.* p. 488). The element is thus non-metallic (see Comparison with nitrogen and with sulphur, p. 564).

**Occurrence.** — This element is found in nature in the form of phosphates. Calcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$  forms 26 per cent of the bones and teeth, and it occurs in all fertile soils. It constitutes a large part of the "phosphate rock" of Georgia, Florida, the Carolinas, Tennessee, and of Algeria and Tunis. A conspicuous mineral related to this substance, apatite (Gk. *aparádō*, I cheat),  $\text{Ca}_5\text{F}(\text{PO}_4)_3$  and  $\text{Ca}_5\text{Cl}(\text{PO}_4)_3$ , is found in large quantities in Canada, and is a component of many rocks. Complex organic compounds of phosphorus, such as lecithin and some proteins, are essential constituents of the muscles, the nerves, and the brain. Amongst foods, egg-yolks and beans contain a large proportion.

**Preparation.** — Brand, merchant and alchemist, of Hamburg, discovered phosphorus (1669) by distilling the residue from evaporated urine, in the course of his search for the Philosopher's stone. The mode of preparing it from bone-ash was first published by Scheele (1771). Green bones, after the gelatine has been extracted from them, by means of water boiling under pressure, are subjected to destructive distillation, a process which yields bone-oil. The residue is a mixture

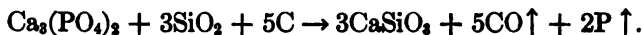
of carbon (*q.v.*) and calcium phosphate. It is used by sugar renners as a decolorizer. When its powers in this direction have been exhausted, it is **calcined** — that is to say, all the combustible matter is burned out of it, — and the product is bone-ash, which contains about 83 per cent of calcium phosphate. Formerly this was used in making phosphorus, but now the less expensive calcium phosphate of fossil origin is employed.

A mixture of powdered bone-ash or calcium phosphate and sulphuric acid (sp. gr. 1.5 to 1.6) is heated with steam and stirred in a wooden vat:  $\text{Ca}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{H}_3\text{PO}_4 + 3\text{CaSO}_4 \downarrow$ . The calcium sulphate is partly precipitated during the heating. The liquid obtained by filtration is evaporated in leaden pans. During this process most of the remainder of the calcium sulphate is deposited and a syrupy, crude phosphoric acid is obtained. This acid is mixed with sawdust, or carbon in some form, and the mixture is first dried and then distilled in earthenware retorts. The phosphoric acid first loses water and turns into metaphosphoric acid, then the latter is reduced by the carbon, carbon monoxide and phosphorus vapor passing off:



A white heat is required for the distillation, and a pipe from the tubular clay retort conducts the vapors into cold water, in which the phosphorus collects.

A much simpler and more modern process depends on the use of the electric furnace (Fig. 125). The calcium phosphate is mixed with the proper proportions of carbon and silicon dioxide (sand), and the mixture is introduced continuously into the furnace. The discharge of an alternating current between carbon poles produces the very high temperature which the action requires. The calcium silicate which is formed fuses to a slag, and can be withdrawn at intervals. The gaseous products pass off through a pipe and the phosphorus is caught under water:



We may regard the phosphate as being composed of two oxides,  $3\text{CaO}$ ,  $\text{P}_2\text{O}_5$ . It thus appears that the calcium oxide has united with the

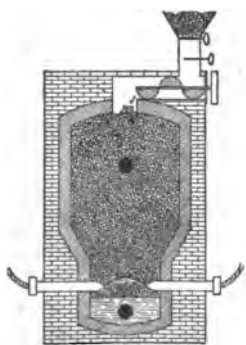


FIG. 125.

silica, which is an acid anhydride (*cf.* p. 431):  $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$ , while the phosphoric anhydride has been reduced.

The phosphorus, after purification, is cast into sticks in tubes of tin or glass, standing in cold water.

**The Electric Furnace.** — By an electric furnace is understood an electro-thermal arrangement in which the heat produced by some resistance offered to the current, such as that of an air-gap between the carbons, is used to produce chemical change. Electrolysis plays no part in the phenomena, and an alternating current, which can produce no electrolytic decomposition, is generally employed. The restricted area within which the heat is developed makes possible the attainment of a high temperature (see Calcium carbide).

**Physical Properties.** — There are at least two allotropic forms (p. 315) of phosphorus, known as white phosphorus and red phosphorus. **White phosphorus**, prepared as described above, is at first transparent and colorless, but after exposure to light acquires a superficial coating of the red variety. Its density is 1.83. It melts at  $44^\circ$ , and boils at  $287^\circ$ . Its molecular weight at  $313^\circ$  is 128, and at a red heat 119.8. As the atomic weight is 31, the formula, within this range, is  $\text{P}_4$ . At  $1700^\circ$  the value 91.2 indicates a partial dissociation into  $\text{P}_2$ . In solution the formula is  $\text{P}_4$ . White phosphorus is very soluble in carbon disulphide, less soluble in ether and other organic solvents, and insoluble in water. It is exceedingly poisonous, less than 0.15 g. being a fatal dose, and is an ingredient in roach paste and rat poison (a mixture with lard as solvent, and flour). Continued exposure to its vapor causes necrosis, a disease from which matchmakers are liable to suffer. The jawbones and teeth are particularly liable to attack.

**Red phosphorus** is a red powder consisting in part of small tabular crystals. It is obtained by heating white phosphorus to about  $250^\circ$  in a vessel from which air is excluded. The change is much more rapid at slightly higher temperatures. Since a great amount of heat is evolved in the transformation, the phosphorus is closely confined to prevent volatilization. A trace of iodine accelerates the transformation, and it then takes place even in the cold.

Red phosphorus does not melt, but passes directly into vapor. Its vapor is identical with that of white phosphorus. It is insoluble in carbon disulphide and other solvents. It is not poisonous, and, unlike white phosphorus, does not require to be kept under water to

avoid spontaneous combustion. Its melting-point, in a closed vessel, varies, being  $550^{\circ}$  when heated very slowly, and  $600^{\circ}$  when heated rapidly. This shows that it is a solid solution, probably of the white variety in a less active kind. Hence, its properties are variable, *e.g.*, density from 2.05 to 2.34. Bridgeman, by heating white phosphorus at  $200^{\circ}$  under a pressure of 1200 kg./cm.,<sup>2</sup> has obtained a black, lustrous phosphorus (sp. gr. 2.69), which is a third variety, and has a fair electrical conductivity.

**Chemical Properties of White Phosphorus.**—White phosphorus unites directly with the halogens with great vigor. It unites slowly with oxygen in the cold, and with sulphur and many metals when the materials are heated together. The slow union of cold phosphorus with atmospheric oxygen is accompanied by the evolution of light, although the temperature is not such as we usually associate with incandescence. Hence the word phosphorescence. The name of the element (Gk.  $\phi\acute{\omega}\varsigma$ , light;  $\phi\acute{\epsilon}\phi\omega$ , I bear) records this property. Apparently the chemical energy, transformed in connection with the oxidation, is converted, in part at least, into radiant energy instead of completely into heat.\* A curious fact in connection with the luminosity and concomitant oxidation of phosphorus is that these occurrences depend upon the concentration of the oxygen gas as well as upon the temperature. Thus, phosphorus does not shine or oxidise in pure oxygen below  $27^{\circ}$ . If the concentration of the oxygen is reduced to 200 mm. or less by means of a pump, or by mixing with an indifferent gas such as nitrogen, phosphorescence becomes perceptible at the ordinary temperature. This explains the luminosity shown in the air. At lower temperatures, lower pressures have to be used. The phosphorescence may be destroyed by the vapor of turpentine and other substances. All these phenomena are probably due to the intermediate formation of phosphorus trioxide, the vapor of which shows the same effects. The slow oxidation of phosphorus is accompanied by the production of ozone, but the nature of the action is still unknown (*cf.* p. 311).

\* The same production of light from chemical action in a cold body is seen in the luminosity of certain parts of fireflies and some species of fish. In many violent chemical changes the light given out is conspicuously more intense than that proper to the temperature produced (*cf.* p. 94), and must come, therefore, in part, directly from the chemical energy. Thus, burning magnesium has a temperature of about  $1350^{\circ}$ , while the production of light of the same character by mere incandescence, would require a temperature of about  $5000^{\circ}$ .

The difference in behavior of pure and diluted oxygen may be shown by pouring a solution of phosphorus in carbon disulphide on to two strips of filter paper. One of the strips, hung in the air, catches fire as soon as the evaporation of the solvent has exposed a large area of finely divided phosphorus. The other, hung in a jar of oxygen, remains unaffected, but becomes ignited instantly upon removal from the jar [Lect. exp.].

**Chemical Properties of Red Phosphorus.** — This variety of the element, since it is formed with evolution of heat, contains less energy than does white phosphorus and is much less active. It does not catch fire in the air below  $240^{\circ}$ , while ordinary phosphorus ignites at  $35\text{--}45^{\circ}$ . Indeed, it is the vapor that begins to combine with oxygen, and this behavior is only an independent proof of the low vapor tension of the red variety. When the vapor tension of white phosphorus has reached 760 mm. (at  $287^{\circ}$ , the b.-p.), that of red phosphorus is almost imperceptible.

Red phosphorus is to be regarded as the normal, stable form of phosphorus. The fact that yellow phosphorus can be kept a great length of time, and is changed but slowly on exposure to light, only shows that the transformation into a stabler condition is retarded by the lowness of the temperature (cf. p. 126). The relation between the two varieties of phosphorus is quite distinct from that between rhombic and monoclinic sulphur (p. 411). In the latter case there is a definite temperature of transformation ( $96^{\circ}$ ) above which one form completely disappears, and below which the other form is incapable of permanent existence. With the varieties of phosphorus no such point of transformation exists, because with phosphorus the two forms are miscible, while with sulphur they are not. It is only by condensing the vapor that the yellow kind is obtained. The production from the vapor (also  $P_4$ ) of the white solid at low temperatures, instead of the red solid whose formation would be accompanied by a larger liberation of heat, is simply an illustration of the principle of transformation by steps (p. 544). At  $1200^{\circ}$ , however, the vapor deposits red phosphorus.

The term **allotropic modifications** is applied to oxygen and ozone (q.v.) which are certainly, and to red and white phosphorus which are, probably, chemically distinct substances. It is used also of rhombic and monoclinic sulphur, where the difference is purely physical. But it is applied only to simple substances, although many compounds show several forms (cf. Ammonium nitrate), exactly as does sulphur. In short, it has at present no scientific value, for it covers a heterogeneous mass of phenomena which, in part, still await elucidation. If **allotropic modifications** were to be defined as **substances** (p. 4) **composed**

of the same materials, but possessing different proportions of free or available energy, and, therefore, different physical properties and different degrees of chemical activity, which is apparently the sense in which the expression is commonly employed, then ice, water, and steam would be examples of such substances. In each of the above four illustrations, the second (in the case of water, the third) is the more active form.

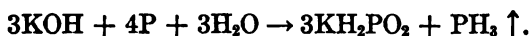
**Uses of Phosphorus, Matches.**—The greater part of the phosphorus of commerce is employed in the manufacture of matches. The first articles of this sort (1812) were sticks coated with sulphur and tipped with a mixture of potassium chlorate and sugar. For ignition they were dipped into a bottle containing asbestos moistened with concentrated sulphuric acid. Matches involving the use of phosphorus (1827) have now displaced all others. In making common matches which strike on any rough surface, the sticks are first dipped in melted sulphur or paraffin to the extent of about half an inch. The head is often composed of manganese dioxide or lead dioxide  $PbO_2$ , and a little potassium chlorate, which supply oxygen, a small proportion of white phosphorus, or of a sulphide of phosphorus  $P_4S_3$  which is readily ignited by friction, and antimony trisulphide (combustible) with dextrine or glue. A paste made of these materials is spread evenly upon a slab, and the prepared sticks fixed in a frame are dipped once or twice in the mixture. On account of the danger of necrosis amongst the workers, the use of white phosphorus is forbidden by law in Sweden, France, Great Britain, and Switzerland, and is prevented by a tax of two cents per 100 matches in the United States.

In the case of "safety" matches, the mixture upon the head is not easily ignited by itself. It is composed of potassium chlorate or dichromate, some sulphur or antimony trisulphide, and a little powdered glass to increase the friction, all held together with glue. Upon the rubbing surface on the box is a thin layer of antimony trisulphide mixed with red phosphorus and glue. The friction converts a little of the red phosphorus into vapor, which catches fire readily. To prevent smoldering of the burned matches, the upper ends of the sticks are sometimes soaked in a solution of alum or sodium phosphate.

**Phosphine.**—Three hydrides of phosphorus are known. These are, phosphine  $PH_3$  (a gas), a liquid hydride  $P_2H_4$ , which is presumably the analogue of hydrazine  $N_2H_4$ , and a solid hydride  $P_3H_3$ .

Phosphine  $PH_3$  does not seem to be produced under ordinary circumstances by the direct union of the elements. It is formed

slowly, however, with active hydrogen, from zinc and hydrochloric acid at 70°, and white phosphorus. The gas may be made by boiling white phosphorus with potassium hydroxide solution in an apparatus similar to that used for generating hydrogen. Potassium hypophosphite is formed at the same time:



The gas made in this fashion contains a little of the vapor of the liquid hydride, which is spontaneously inflammable, and consequently the bubbles of the mixture catch fire when they reach the surface of water in the trough:  $\text{PH}_3 + 2\text{O}_2 \rightarrow \text{H}_3\text{PO}_4$ . In still, moist air, the fog of droplets of phosphoric acid solution form smoke rings. To avoid explosions, the air in the flask must be displaced by hydrogen or illuminating-gas before heat is applied. This product contains also free hydrogen, in increasing quantities as the action goes on, in consequence of the reduction of the water and potassium hydroxide by the potassium hypophosphite:  $\text{KH}_2\text{PO}_2 + \text{KOH} + \text{H}_2\text{O} \rightarrow \text{K}_2\text{HPO}_4 + 2\text{H}_2$ . Potassium phosphate is formed.

The simplest method of preparing the gas is by the action of water upon calcium phosphide:



This action is analogous to that of water upon magnesium nitride (p. 514), by which ammonia is produced. In consequence of the fact that calcium phosphide is a substance of irregular composition, a mixture of all three hydrides is generally obtained. By passing the gas through a strongly cooled delivery tube, however, the liquid compound is condensed and fairly pure phosphine passes on.

Phosphine is a colorless gas, which is easily decomposed by heat into its elements. It is exceedingly poisonous and, unlike ammonia, it is insoluble in water, and produces no basic compound corresponding to ammonium hydroxide when brought in contact with this substance. It resembles ammonia, formally at least, in uniting with the hydrogen halides (see below). It differs from ammonia, however, inasmuch as it does not unite with the oxygen acids. Phosphine acts upon solutions of some salts, precipitating phosphides of the metals:



The liquid hydrogen phosphide boils at 57°. The molecular weight, as determined by the density of its vapor, shows the formula to



be  $P_2H_4$ . It forms no salts, and is therefore quite unlike hydrazine. When exposed to light, it decomposes, giving phosphine and the solid hydride.

**Phosphonium Compounds.**—Hydrogen iodide unites with phosphine to form a colorless solid, crystallizing in beautiful, highly refracting, square prisms:  $PH_3 + HI \rightarrow PH_4I$ . Hydrogen chloride combines similarly with phosphine, but only when the gases are cooled by a freezing mixture, or are brought together under a total pressure of 18 atmospheres at  $14^\circ$ . When the pressure is released, rapid dissociation occurs. This dissociation is one of the many cases where an action which absorbs heat, nevertheless goes on spontaneously (cf. p. 35). The indispensable fall in the energy of the system takes place by virtue of the expansion of the constituents, and in amount this more than offsets the heat acquired.

In imitation of the ammonia nomenclature, these substances are called **phosphonium iodide** and **phosphonium chloride**  $PH_4Cl$ . They are entirely different, however, from the corresponding ammonium derivatives, for the  $PH_4^+$  ion is unstable. When brought in contact with water, they decompose into their constituents, the hydrogen halide going into solution, and the phosphine being liberated as a gas.

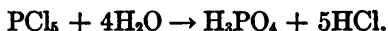
**Halides of Phosphorus.**—The existence of the following halides has been proved conclusively:

			$P_2I_4$ (solid)
$PF_3$ (gas)	$PCl_3$ (liquid)	$PBr_3$ (liquid)	$PI_3$ (solid)
$PF_5$ (gas)	$PCl_5$ (solid)	$PBr_5$ (solid)	.....

These substances may all be formed by direct union of the elements. They are incomparably more stable than are the similar compounds of nitrogen. They are all completely hydrolyzed by water, and each gives an oxygen acid of phosphorus and the hydrogen halide (see below). This action was used in the preparation of hydrogen bromide (p. 272) and hydrogen iodide (p. 278).

**Phosphorus trichloride**  $PCl_3$  is made by passing chlorine gas over melted phosphorus in a flask until the proper gain in weight has occurred. It is a liquid, boiling at  $76^\circ$ . When excess of chlorine is employed, **phosphorus pentachloride**  $PCl_5$ , which is a white solid body, is formed. When moist air is blown over any of these substances, the water is condensed to a fog by the hydrogen halide. In

the case of the interaction of phosphorus pentachloride and water, phosphoric acid is formed:



With a limited supply of water the hydrolysis is not so complete, and phosphoryl chloride\* (phosphorus oxychloride), a liquid boiling at  $107^\circ$ , is produced:  $\text{PCl}_5 + \text{HOH} \rightarrow \text{POCl}_3 + 2\text{HCl}$ .

This interaction of phosphorus pentachloride and water is a perfectly general one, and takes place with most compounds containing hydroxyl. Thus, when alcohol (which differs from water in having ethyl  $\text{C}_2\text{H}_5$ , instead of hydrogen, combined with hydroxyl) is poured upon it, ethyl chloride, phosphoryl chloride, and hydrogen chloride are formed:



The same action takes place with all carbon compounds containing hydroxyl, and is used as a means of showing the presence of this group in their structure. The reaction is shown by inorganic compounds also. Thus, anhydrous sulphuric acid gives sulphuryl chloride, which may be separated from the phosphoryl chloride by fractional distillation (see Petroleum):



Phosphorus pentachloride, when heated, reaches a vapor tension of 760 mm. at  $163^\circ$ , and while still solid. It therefore passes freely into vapor (boils, so to speak) at this temperature, and condenses directly to the *solid* form. This sort of distillation is called **sublimation**. At a pressure above that of the atmosphere it melts at  $166^\circ$ . This is simply a case in which the vapor tension of the solid, increasing with rise in temperature, happens to pass the arbitrary value of the opposing pressure (one atmosphere) peculiar to experiments carried on in open vessels, before the melting-point is reached. The same phenomenon is shown by sulphur trioxide (p. 430).

Phosphorus pentachloride (*cf.* p. 260) and pentabromide, when vaporized, are partially dissociated:



Since the first two members of this equilibrium are colorless, while the bromine is brown, this action may be used to **illustrate** the effect upon

\* This substance is a mixed anhydride (p. 449) of phosphoric acid and hydrogen chloride.

a system, of **increasing the concentration of one of the interacting substances** (p. 291). Two tubes of equal volume and containing equal amounts of the pentabromide are prepared. A small amount of the tribromide is added to the second, and both are sealed up. When the tubes are now heated to the same temperature, the contents of the second will be less strongly colored by bromine in consequence of the greater activity in it of the reversing action. At  $163^{\circ}$  and 760 mm., about 4 per cent of the molecules of the vapor of the pentachloride are dissociated into the trichloride and chlorine.

**Oxides of Phosphorus.**—The oxides of phosphorus are the so-called trioxide  $P_4O_6$ , the pentoxide  $P_2O_5$ , and a tetroxide  $P_2O_4$ .

The **pentoxide** is a white powder formed when phosphorus is burned with a free supply of oxygen. It unites with water with great violence to form metaphosphoric acid (see below), and hence is known as **phosphoric anhydride**:  $P_2O_5 + H_2O \rightarrow 2HPO_3$ . In the laboratory this action is frequently utilized for drying gases (p. 123) and for removing water from combination (p. 527). The vapor density of the pentoxide indicates that its formula is  $P_4O_{10}$ , use of which, however, would only complicate our equations.

The **trioxide**  $P_4O_6$  is obtained by burning phosphorus in a tube with a restricted supply of air. It is a white solid, melting at  $22.5^{\circ}$  and boiling at  $173^{\circ}$ . On account of the ease with which it may be volatilized, it can be separated by distillation from any pentoxide formed at the same time. The operation must be carried out in an apparatus from which the air is excluded, as the trioxide unites spontaneously with oxygen. The vapor is phosphorescent (p. 550). The vapor density of the substance shows that its formula is  $P_4O_6$ . This formula is preferred to the simpler one because, although the oxide is the anhydride of phosphorous acid, it nevertheless unites exceedingly slowly with cold water to form this substance. It interacts vigorously with hot water, but phosphine, red phosphorus, hypophosphoric acid, and phosphoric acid are amongst the products, and very little phosphorous acid escapes decomposition. When this oxide is heated to  $440^{\circ}$  it decomposes, giving the tetroxide  $P_2O_4$  and red phosphorus.

**Acids of Phosphorus.**—There are six different acids of phosphorus in which four distinct stages of oxidation are shown. The highest stage is represented by three phosphoric acids, where the degree of hydration of the anhydride varies. The others show

three different and lower states of oxidation (study their positive and negative valences, p. 494):

Orthophosphoric acid	$\text{H}_3\text{PO}_4$ (= $3\text{H}_2\text{O}, \text{P}_2\text{O}_5$ )
Pyrophosphoric acid	$\text{H}_4\text{P}_2\text{O}_7$ (= $2\text{H}_2\text{O}, \text{P}_2\text{O}_5$ )
Metaphosphoric acid	$\text{HPO}_3$ (= $\text{H}_2\text{O}, \text{P}_2\text{O}_5$ )
Hypophosphoric acid	$\text{H}_2\text{PO}_3$ (= $2\text{H}_2\text{O}, \text{P}_2\text{O}_4$ )
Phosphorous acid	$\text{H}_2\text{PO}_3$ (= $3\text{H}_2\text{O}, \text{P}_2\text{O}_3$ )
Hypophosphorous acid	$\text{H}_3\text{PO}_3$ (= $3\text{H}_2\text{O}, \text{P}_2\text{O}$ )

**The Phosphoric Acids.** — The relation between the three different phosphoric acids may be seen by considering them as being formed from phosphorus pentoxide and water. It will be remembered that in the majority of cases already considered, this sort of action takes place for the most part in but one way. Thus, nitric acid is known in but one form, which is produced by the union of one molecule each of nitrogen pentoxide and water:  $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$ . Similarly the chief sulphuric acid is the one formed from one molecule of sulphur trioxide and one molecule of water:  $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ , although here we have both the hydrate  $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ , which might be written  $\text{H}_4\text{SO}_5$  and disulphuric acid  $\text{H}_2\text{S}_2\text{O}_7$ . Referred to the anhydride these three acids are  $\text{H}_2\text{O}, \text{SO}_3$ ,  $2\text{H}_2\text{O}, \text{SO}_3$ , and  $\text{H}_2\text{O}, 2\text{SO}_3$ . Periodic acid (p. 487) has a set of even more complexly related acids or salts.

Now, when phosphoric anhydride acts upon water we obtain a solution which, on immediate evaporation, leaves a glassy solid,  $\text{HPO}_3$ , known as **metaphosphoric acid**. This is  $\text{H}_2\text{O}, \text{P}_2\text{O}_5$ . When, however, the solution is allowed to stand for some days, or is boiled with a little dilute nitric acid, the hydrogen-ion of which acts catalytically, the residue from evaporation is  $\text{H}_3\text{PO}_4$ , **orthophosphoric acid**  $3\text{H}_2\text{O}, \text{P}_2\text{O}_5$ :

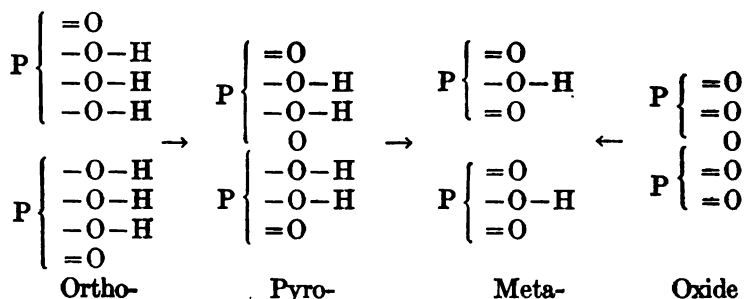


Conversely, when orthophosphoric acid is kept at about  $255^\circ$  for a time, it slowly loses water, and  $\text{H}_4\text{P}_2\text{O}_7$ , **pyrophosphoric acid**, is obtained:



This acid is  $2\text{H}_2\text{O}, \text{P}_2\text{O}_5$ . Further desiccation leaves metaphosphoric acid, which cannot be further resolved into phosphorus pentoxide and water. When dissolved in water, pyrophosphoric acid slowly resumes the water which it has lost and gives the ortho-acid again.

The relations of all these substances are more clearly seen in the graphic formulæ:



The addition or removal of water leaves the valence, and therefore the degree of oxidation, of the phosphorus unchanged.

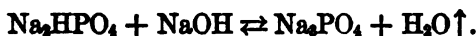
Pyrosulphuric acid and its salts when dissolved in water give sulphuric acid and acid sulphates, respectively. That is to say, the ion  $\text{S}_2\text{O}_7$  is not capable of existence. But the very slow rate at which the less hydrated phosphoric acids change into the more hydrated ones shows that ions like  $\text{PO}_4^{3-}$ ,  $\text{PO}_3^{-}$ , and  $\text{P}_2\text{O}_7^{4-}$  may be comparatively stable. The behavior of solutions of the salts shows this even more clearly.

**Orthophosphoric Acid  $\text{H}_3\text{PO}_4$ .**—As we have seen (p. 548), ordinary calcium phosphate is the source of the impure, commercial acid. Pure orthophosphoric acid may be made by boiling red phosphorus with slightly diluted nitric acid and evaporating off the water and excess of nitric acid. The product is a white, crystalline deliquescent **hemihydrate**,  $2\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$  (m.-p.  $29.35^\circ$ ). Anhydrous orthophosphoric acid melts at  $42.3^\circ$ .

This acid is **much weaker** than sulphuric acid, and is dissociated chiefly into the ions  $\text{H}^+$  and  $\text{H}_2\text{PO}_4^-$ . The dihydrophosphate-ion is broken up to some extent into  $\text{H}^+$  and  $\text{HPO}_4^{2-}$ , as we learn from the fact that the solution of the sodium salt  $\text{NaH}_2\text{PO}_4$  is acid. The ion  $\text{HPO}_4^{2-}$  is hardly dissociated at all, for a solution of the salt  $\text{Na}_2\text{HPO}_4$  is not acid in reaction.

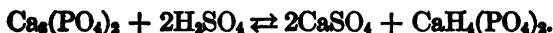
**Salts of Orthophosphoric Acid.**—As a **tribasic acid**, it forms salts of three kinds, such as  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , and  $\text{Na}_3\text{PO}_4$ . These are known respectively as **primary**, **secondary**, and **tertiary** sodium orthophosphate. The primary sodium phosphate is faintly

acid in reaction. The secondary one is slightly alkaline, because of hydrolysis arising from the tendency of the hydrogen-ion of the water to combine with the  $\text{HPO}_4^-$  to form  $\text{H}_2\text{PO}_4^-$ , which is much more feebly acid than is phosphoric acid  $\text{H}_3\text{PO}_4$ . The simplified equation (p. 419) shows the reason for the alkalinity of the solution:  $\text{HPO}_4^- + \text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{OH}^-$ , for hydroxyl-ion is present. The tertiary phosphate is stable only in solid form, and can be made by evaporating to dryness a mixture of the secondary phosphate and sodium hydroxide:

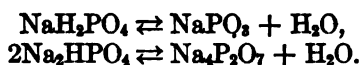


When the product is dissolved in water, the action is reversed (cf. p. 418). Mixed phosphates are also known, particularly sodium-ammonium phosphate (*microcosmic salt*)  $\text{NaNH}_4\text{HPO}_4$ , and the insoluble magnesium-ammonium phosphate,  $\text{MgNH}_4\text{PO}_4$ .

Primary calcium phosphate, known in commerce as *superphosphate*, is used as a fertilizer. Since plants can take up soluble substances only, the insoluble, natural calcium phosphate is of relatively little service to plants. It is therefore converted into the superphosphate, which is soluble, by treatment with dilute sulphuric acid:



The tertiary phosphates are unchanged by heating. The primary and secondary phosphates, however, retaining, as they do, some of the original hydrogen of the phosphoric acid, are capable of losing water like phosphoric acid itself, when heated. The actions are slowly reversed when the products are dissolved in water:



It will be seen that the meta- and pyrophosphates of sodium are formed by these actions; and this is indeed the simplest way of forming these substances, since the acids themselves are not permanent in solution, and are too feeble to lend themselves to exact neutralization. Ammonium salts of phosphoric acid lose ammonia, as well as water, when heated (cf. p. 520). Thus, *microcosmic salt* gives first the primary sodium phosphate:



and this in turn loses water to give the metaphosphate.

**Pyrophosphoric Acid  $H_4P_2O_7$ .** — This acid, obtained by heating orthophosphoric acid, may be prepared in pure form by making the sparingly soluble lead salt from sodium pyrophosphate, and precipitating the lead-ion as lead sulphate by addition of sulphuric acid. In solution it gradually reunites with water. Although tetrabasic, having four hydrogen atoms which may be displaced by metals, only two kinds of salts are known. These are the normal salts, such as  $Na_4P_2O_7$ , and those in which one-half of the hydrogen has been displaced by a metal, such as  $Na_2H_2P_2O_7$ .

**Metaphosphoric Acid  $HPO_3$ .** — This is the "glacial phosphoric acid" of commerce, and is usually sold in the form of transparent sticks. It is obtained by heating orthophosphoric acid, or by direct union of phosphorus pentoxide with a small amount of cold water. It passes into vapor at a high temperature, and its vapor density corresponds to the formula  $(HPO_3)_2$ . The existence of certain complex salts confirms our belief in the existence of association (p. 282).

**Sodium metaphosphate  $NaPO_3$ ,** in the form of a small globule obtained by heating microcosmic salt on a platinum wire, is used in analysis. When minute traces of oxides of certain metals are placed upon such a globule, known as a **bead**, and heated in the Bunsen flame, the mass is colored in various tints according to the oxide used (**bead test**). This action may be understood when we consider that sodium metaphosphate takes up water to form primary sodium orthophosphate:  $NaPO_3 + H_2O \rightarrow NaH_2PO_4$ . In the same way, but at higher temperatures, it is able to take up oxides of elements other than hydrogen, giving mixed orthophosphates. Thus, with oxide of cobalt, a part of the metaphosphate unites according to the equation:

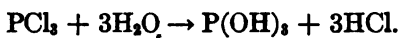


and the product gives a blue color to the bead.

**Distinguishing Tests.** — When a solution of **nitrate of silver** is added to a solution of orthophosphoric acid or any soluble orthophosphate, a yellow precipitate of silver orthophosphate  $Ag_3PO_4$  is produced. This is a test for orthophosphate-ion. With pyrophosphoric acid or any pyrophosphate the product is white  $Ag_4P_2O_7$ . With metaphosphoric acid a white precipitate,  $AgPO_3$ , is obtained also. Metaphosphoric acid coagulates a clear solution (really a colloidal suspension) of albumen (say, white of egg), while ortho- or pyrophosphoric acid has no visible effect upon it.

A test for orthophosphoric acid, or rather the ion  $\text{PO}_4^{\equiv}$ , consists in adding a drop of the solution containing this ion to a solution of ammonium molybdate (*q.v.*) in dilute nitric acid. A copious yellow precipitate of an ammonium phosphomolybdate  $(\text{NH}_4)_3\text{PO}_4 \cdot 11\text{MoO}_3 \cdot 6\text{H}_2\text{O}$  appears on warming. In presence of excess of ammonia, the formation of the white insoluble ammonium-magnesium phosphate (p. 559) serves as a test also. Arsenic acid (*q.v.*) gives precipitates of appearance and composition similar to these two.

**Phosphorous Acid  $\text{H}_3\text{PO}_3$ .** — With cold water phosphorus trioxide  $\text{P}_4\text{O}_6$  yields phosphorous acid very slowly. With hot water the action is exceedingly violent and complex (p. 556). This acid may be obtained also by the action of water upon phosphorus trichloride, tribromide, or tri-iodide and evaporation of the solution:

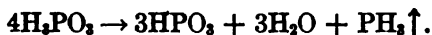


Some of this acid, along with phosphoric acid and hypophosphoric acid, is formed when moist phosphorus oxidizes in the air.

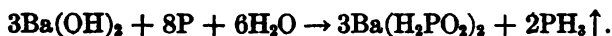
In spite of the presence of three hydrogen atoms, this acid is dibasic, and two only are replaceable by metals. To express this fact, the first of the following formulæ is preferred:



since the symmetrical formula would indicate no difference between the three hydrogen atoms. H united directly to P, as here and in  $\text{PH}_3$ , is practically not acidic. Phosphorous acid is a powerful reducing agent, precipitating silver, for example, in the metallic form from solutions of its salts. When heated, it decomposes, giving the most stable acid of phosphorus (*cf.* pp. 447, 474, 483), namely, metaphosphoric acid, and phosphine:



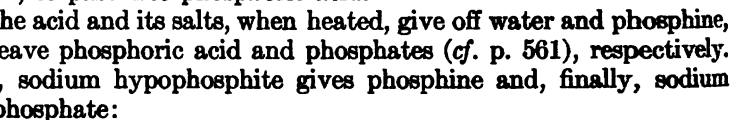
**Hypophosphorous Acid.** — The potassium salt of this acid is obtained, as we have seen, when phosphorus is heated with potassium hydroxide solution (p. 553). It may be prepared in the free form by substituting barium hydroxide for potassium hydroxide:





By careful addition of dilute sulphuric acid to the resulting liquid, barium sulphate is precipitated. On evaporation of the water, the white crystalline acid  $\text{H}_2\text{PO}_3$  is obtained. This acid is monobasic; two of its hydrogen atoms cannot be displaced by metals. To express this fact the graphic formula  $\text{O} = \text{P} \begin{cases} - \text{H} \\ - \text{H} \\ - \text{OH} \end{cases}$  is used. This substance is also a powerful reducing agent, tending, by the acquisition of oxygen, to pass into phosphoric acid.

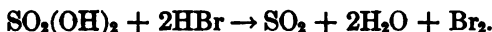
The acid and its salts, when heated, give off water and phosphine, and leave phosphoric acid and phosphates (cf. p. 561), respectively. Thus, sodium hypophosphite gives phosphine and, finally, sodium pyrophosphate:



**Hypophosphoric Acid  $\text{H}_2\text{PO}_3$ .**—When white phosphorus is heated under nitric acid, alone, orthophosphoric acid is formed. When, however, cupric nitrate (or silver nitrate; other nitrates are without effect) is added, copper is precipitated (as  $\text{Cu}_3\text{P}_2$  or  $\text{Cu}$ ). By neutralizing half of the resulting solution with sodium carbonate, and adding the other half, a copious precipitate of a hydrate of sodium hypophosphate  $\text{NaHPO}_3 \cdot 2\text{H}_2\text{O}$  appears. From this salt, other salts and the free acid can be prepared.

**Structural Formulæ of Salts of Hydrogen.**—As a rule, the formulæ of acids have thus far been written with the ionizable hydrogen in front:  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCO}_2\text{CH}_3$ . This is only one illustration of the method by which chemists have constantly sought to utilize formulæ for the purpose of expressing, not merely the composition of a substance, but some of its properties as well. By another typographical device we have attempted to indicate the behavior of dilute solutions by putting the radicals in brackets:  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Ba}(\text{OH})_2$ . These are called reaction formulæ, and their object is to exhibit the modes of action of the substance. Now the modes of action of a single substance are often rather various, and one and the same structural formula cannot represent all of these at once. We have observed this, particularly, with the oxygen acids. Thus,  $\text{H}_2\text{SO}_4$  expresses the mode of activity in dilute solution and often when no solvent is present, as in the action on chlorides (p. 206) and nitrates (p. 526). But when all the hydrogen of an acid is not ioniz-

able, we regard that which is so as part of an hydroxyl group in the parent molecules, and the rest as being attached to the characteristic non-metal of the acid, as, for example, in phosphorous acid (p. 561; cf. pp. 442, 540). Thus, we should write phosphorous acid  $\text{HPO}(\text{OH})_2$ , instead of  $\text{H}_2\text{PO}_3\text{H}$ , to chronicle this fact. So also the formula  $\text{POH}_2(\text{OH})$  is used for hypophosphorous acid. Molecular actions, such as those of sulphuric acid  $\text{SO}_2(\text{OH})_2$  (p. 272), are well shown by these formulæ:

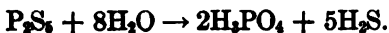


It must be noted particularly that this sort of formula, when the substance for which it stands is an acid, represents only some features in the behavior of the anhydrous substance and of the molecules, and not the ionic action in solution. A formula like  $\text{Ba}(\text{OH})_2$ , where the material is a base, on the other hand, represents both the ionic and the molecular behavior. The graphic formula is more general (cf. p. 540). It shows all these relations, and often still others, but none of them so specifically.

**Sulphides of Phosphorus.**—White phosphorus, when heated with sulphur unites with explosive violence. By using red phosphorus the action can be controlled. By employing the proper proportions, the **pentasulphide**  $\text{P}_2\text{S}_5$  is secured. It is purified by distillation from a retort in which a current of carbon dioxide is maintained (see below). The distillate solidifies to a yellow, crystalline solid (m.-p.  $290^\circ$ , b.-p.  $515^\circ$ ). Materials undergoing chemical change, which are to be kept at a constant, high temperature, are often placed in tubes suspended in the vapor of the pentasulphide. When a lower temperature is required, boiling sulphur ( $445^\circ$ ) is used.

**Distillation in a stream of some inactive gas** is a common means of distilling under reduced pressure (cf. p. 316). The dilution of the vapor lowers its partial pressure, just as would evacuation. This plan has the advantage, however, of sweeping the vapor away from the heated region into the condenser, and so diminishing the amount of decomposition. In dealing with compounds of carbon, a current of steam is often used for the above purposes. It enables us also to separate a slightly volatile substance from one which is almost involatile.

Phosphorus pentasulphide is hydrolyzed by cold water, and acts upon other substances containing hydroxyl when heated with them, the actions being similar to those of the pentachloride (p. 555):



Other sulphides,  $P_4S_3$  (used in making matches, p. 552), and  $P_4S_7$ , may be prepared by using the constituents in the proportions represented by these formulæ.

**Comparison of Phosphorus with Nitrogen and with Sulphur.** — Although phosphorus and nitrogen are regarded as belonging to one family, the differences between them are more conspicuous than the resemblances. The latter are confined almost wholly to matters concerned with valence. The differences are seen in the facts that nitrogen is a gas, while phosphorus is a solid occurring in two varieties, and that the former is inactive and the latter active. The contrasts between phosphine and ammonia (pp. 553–554) and between the halides of the two elements (p. 554) have been noted already. The pentoxide of nitrogen decomposes spontaneously; that of phosphorus is one of the most stable of compounds. Nitric acid is very active, both as an acid, and as an oxidizing agent; the phosphoric acids are quite the reverse.

On the other hand, the resemblance of phosphorus to sulphur is marked. Both are solids, existing in several forms. Both yield stable compounds with oxygen and chlorine. The hydrogen compounds interact with salts to give phosphides of metals and sulphides of metals, respectively. Against these must be set the facts, that hydrogen sulphide does not unite with the hydrogen halides at all, while phosphine gives the phosphonium halides, and that phosphoric acid is hard to reduce while sulphuric acid is reduced with comparative ease.

**Exercises.** — 1. Explain the effect of sulphuric acid in setting fire to the earliest matches (p. 552).

2. Make a brief definition of a substance which sublimes (p. 555).

3. Why would a mixture of potassium dichromate and hydrochloric acid (p. 418) be less suitable than nitric acid for making phosphoric acid from red phosphorus?

4. Why is not the tertiary phosphate of sodium (p. 559) decomposed by heating? What tertiary phosphates would be decomposed by this means?

5. Formulate the hydrolyses of the secondary and tertiary sodium orthophosphates as was done for sodium sulphide (p. 418).

6. How should you prepare  $Ca_2P_2O_7$  and  $Ca(PO_3)_2$ ?

7. What product should you confidently expect to find after

heating, (a) sodium phosphite  $\text{Na}_2\text{HPO}_3$ , (b) potassium hypophosphite (p. 561)? Make the equations.

8. Compare the elements chlorine and phosphorus after the manner of the comparisons on p. 564.

9. What are the valences of the non-metals in:  $\text{H}_2\text{S}_2\text{O}_7$ ,  $\text{H}_2\text{Cr}_2\text{O}_7$ ,  $\text{KMnO}_4$ ,  $\text{KH}_2\text{PO}_3$ ,  $\text{H}_2\text{NO}_4$ ,  $\text{NaH}_2\text{PO}_3$ ,  $\text{Na}_2\text{PO}_3$ ? Name these substances.

10. Is it oxidation or reduction, or neither, when we make, (a)  $\text{N}_2\text{O}_4$  from  $\text{HNO}_3$ , (b)  $\text{SO}_2$  from  $\text{H}_2\text{SO}_3$ , (c)  $\text{HPO}_3$  from  $\text{H}_3\text{PO}_3$ , (d)  $\text{H}_2\text{S}_2\text{O}_7$  from  $\text{H}_2\text{SO}_4$ , (e)  $\text{Na}_2\text{SO}_4$  from  $\text{NaHSO}_3$ ?

## CHAPTER XXVIII

### CARBON AND THE OXIDES OF CARBON

**The Chemical Relations of the Element.** — The elements of the carbon family are carbon, silicon, germanium, tin, and lead (see Periodic system). Of these the first two are entirely non-metallic, while the others are metallic elements showing more or less strong resemblances to the non-metals. All these elements are quadrivalent as regards the maximum valence which they exhibit. With the exception of silicon, however, they all form many compounds in which they are bivalent.

The chemistry of the compounds of carbon is an exceedingly extensive and complex subject. It is commonly known as **organic chemistry**, on account of the fact that the majority of the substances composing, and produced by, living organisms are compounds of carbon, and that it was at first supposed that their artificial production, *e.g.*, without the intervention of life, was impossible. But many natural organic products have now been made from simpler ones or from the elements, a process called **synthesis**, and the preparation of the others is delayed only in consequence of difficulties caused by their instability and complexity. On the other hand, thousands of carbon compounds, unknown to animal or vegetable life, including many valuable drugs and dyes, have now been added to the catalogue of chemical compounds. More than 200,000 different compounds containing carbon are known, and thousands are added every year.

The elements entering into carbon compounds are chiefly hydrogen and oxygen. After these come nitrogen, the halogens, and sulphur.

### CARBON

**Occurrence.** — Large quantities of carbon are found in the free condition in nature. The diamond is the purest natural carbon, and at the same time the least plentiful. Graphite, or plumbago, which is the next purest, is found in limited amounts, and is a valuable mineral. Coal occurs in numerous forms, but much of it contains no free carbon. Small quantities of the free element have been found in meteorites.

In combination, carbon is found in marsh-gas, or methane  $\text{CH}_4$ , which is the chief component of natural gas. The mineral oils consist almost entirely of mixtures of various compounds of carbon and hydrogen. Whole geological formations are composed of carbonates of common metals, particularly calcium carbonate or limestone, and a double carbonate of calcium and magnesium, known as dolomite.

**Allotropic Forms of Carbon.** — The allotropic (p. 315) forms of carbon differ very strikingly in their physical properties. The **diamond** (density 3.5) is transparent, crystalline, and very hard. **Graphite** (density 2.3) is black, lustrous, and very soft. **Amorphous carbon** is very variable. Thus lampblack (see p. 596) is a fine powder of nearly pure carbon, charcoal (see p. 610) shows the structure of the wood. These amorphous forms can best be discussed after the materials from which they are formed have been considered.

That all the forms are composed of the same element is shown by the fact that they *all* burn in oxygen to give carbon dioxide. Then, too, when heated strongly in absence of air, diamond and the amorphous forms all turn into graphite. They contain different amounts of chemical energy, however. Thus, when 1 g. of each is burned, diamond gives 7870 cal., graphite 7835 and sugar charcoal (p. 438) 8040. The tendency of most carbon compounds, when heated, to **char**, giving free carbon, is used as a **test**.

**The Diamond.** — Diamonds, which are found chiefly in Brazil and South Africa, are scattered sparsely through metamorphic and volcanic rocks which seem to have undergone secondary changes. They are covered with a crust which entirely obscures their luster, and possess natural crystalline forms belonging to the regular system. A form related to the octahedron (p. 172) is frequently observed. It should be noted that this natural form bears no relation whatever to the pseudo-crystalline shape which is conferred upon the stone by the diamond-cutter. Thus, a "brilliant" possesses one rather large, flat face, which forms the base of a many sided pyramid (Fig. 126, showing two views). This form is given to the stone, in order that the maximum reflection of light from its interior may be produced. The

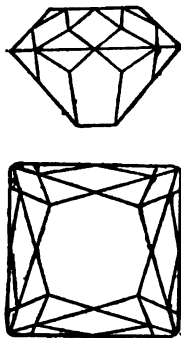


FIG. 126.

diamond is **harder** (see Appendix II) than any other variety of matter, with the exception, perhaps, of one carbide of boron, while only one or two other materials, like carborundum, approach it. Hence, it can be scratched or polished only by rubbing with diamond powder. It is the **densest** form of carbon (density 3.5). The colorless stones, and occasional specimens with special tints (like the blue, Hope diamond) are the most valuable. The black ("carbonado") and discolored specimens are used for grinding and glass cutting. Mounted round the edge of a tube, they are used for drilling rock, so that a cylindrical specimen of the whole of the strata can be secured for examination. All forms of carbon are **insoluble** in all liquids at room temperature. Molten iron (*q.v.*) dissolves five or six per cent, part of which goes into combination. The diamond is a nonconductor of electricity. Diamonds are sold by the new international carat, 200 mgms. (old carat, 4 grains = 205 mgms.), and the value increases with the size. Thus, a first quality, cut stone of 1 carat is worth about \$270, one of 2 carats about \$340 per carat. The largest diamond known, the *Cullinan* (1905), weighed 3032 (old) carats (621 g. or 1.37 lbs). It was presented by the Transvaal government to King Edward VII, and was cut into stones of 516.5 and 309 carats and many smaller ones. Other large stones are the *Nizam* (277 carats), the *Jubilee* (239 carats), and the *Kohinoor* (106 carats).

The diamond, although its origin in nature is still a matter of uncertainty, has been made artificially. Moissan (1887) dissolved carbon in molten iron and, after chilling the mass so as to produce a solid crust, which by its shrinkage severely compressed the interior, allowed the whole to cool very slowly. Portions of the interior of the ingot were treated with acid to dissolve the iron, and amongst the insoluble particles were recognized a few microscopic fragments (none larger than 0.5 mm.) which exhibited the form and hardness of the diamond. The greater part of the carbon, however, appeared, as usual, as graphite.

**Graphite.**— Graphite (Gk. *γράφω*, I write) or plumbago is found in Cumberland, Siberia, Ceylon (1913, 28,500 short tons), Canada, and Austria (1912, 50,000 short tons). It is composed of glittering, slippery scales. Good crystals are seldom found (hexagonal system). The mineral is extremely soft, in utter contrast to the diamond, and has a lower density (2.3). It also conducts electricity. It is now **made artificially** by an electro-thermal process (*cf.* p. 549),

the production in the U. S. being 2542 short tons (1915). A powerful alternating current is passed through a mass of granular anthracite, mixed with pitch and a little sand (Acheson's process). The mixture (3 tons) is piled between the electrodes (Fig. 127) and, on account of its high resistance, becomes strongly heated. The change occupies 24-30 hours.

Graphite is now used exclusively for making the anodes in the electrolytic manufacture of chlorine and in related processes.

Mixed with fine clay it forms the "lead" of lead pencils, first used in the sixteenth century.\* Mixed with clay it is used also for making crucibles, which withstand high temperatures and serve for melting and casting steel and high melting alloys. As "black-lead" it forms stove polish, the layer of fine scales protecting the iron against rusting. It is employed as a lubricant in cases where oil would be decomposed by the heat and where wooden surfaces are in contact.

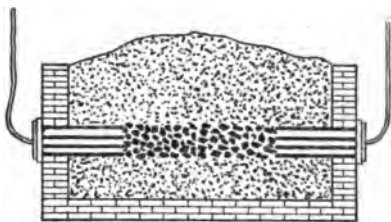


FIG. 127.

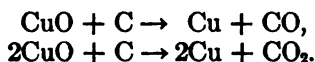
**Chemical Properties of Carbon.** — Diamond, graphite, and amorphous carbon probably differ from one another, not merely in physical properties, but also chemically. Certainly the stability of compounds containing many units of carbon in their molecules indicates a great tendency of carbon to combine with itself, and gives plausibility to the belief that the molecule of free carbon may itself be complex. Differences in the arrangement of the atoms (p. 471) account for the variety in the crystalline forms of the element. Amorphous carbon is the least stable of the three, for it liberates most heat in entering into combination. Since graphite is formed at high temperatures, and diamonds turn into a black mass under the same conditions, we may presume that graphite is the most stable, at least at 3000°.

The most common uses of carbon depend upon its great tendency to **unite with oxygen**, forming carbon dioxide  $\text{CO}_2$ . Under some circumstances carbon monoxide  $\text{CO}$  (see below) is produced. Aside from the direct employment of this action for the sake of the heat which is liberated, it is used also in the **reduction** of ores of iron,

\* Priestley was the first to suggest the use of caoutchouc (raw rubber) as an eraser.



copper, zinc, and many other metals. When, for example, finely powdered cupric oxide and carbon are heated, copper is obtained. The gas given off is either carbon dioxide, or a mixture of this with carbon monoxide, according to the proportion of carbon used:



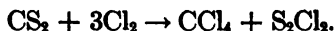
The **union with hydrogen** is ordinarily too slow to be observed. But when the carbon is mixed with pulverized nickel (contact agent), and hydrogen is passed over the mixture at 250°, methane  $\text{CH}_4$  is formed (99 per cent). The action is reversible and exothermal, and is therefore, at higher temperatures, less complete (*cf.* p. 305), at 850° reaching only 1.5 per cent. On the other hand, an electric arc, between carbon poles in an atmosphere of hydrogen, gives traces of acetylene  $\text{C}_2\text{H}_2$  (*q.v.*) this action being endothermal. The other compounds of carbon and hydrogen are all obtained by indirect reactions.

At the high temperatures produced in the electric furnace, carbon **unites with many metals** and some **non-metals**. Compounds formed in this way are known as **carbides**, such as aluminium carbide  $\text{Al}_4\text{C}_3$ , calcium carbide  $\text{CaC}_2$ , and carborundum  $\text{CSi}$  (see below).

**Carbon Disulphide  $\text{CS}_2$ .**— This compound is made by direct union of sulphur vapor and glowing charcoal. An electric furnace like that in Fig. 125 (p. 548) is employed. The substance comes off as a vapor and is condensed.

Carbon disulphide is a colorless, highly refracting liquid (b.-p. 46°). Traces of other compounds give the commercial article a disagreeable smell. It burns in air, forming carbon dioxide and sulphur dioxide. It is an important solvent for sulphur and caoutchouc (rubber), and dissolves iodine and phosphorus freely. Large quantities are employed also in the destruction of prairie dogs and ants, and for freeing grain elevators of rats and mice.

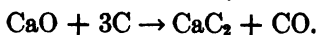
**Carbon Tetrachloride  $\text{CCl}_4$ .**— This compound is manufactured by leading dry chlorine into carbon disulphide containing a little iodine (contact agent) in solution:



The carbon tetrachloride (b.-p. 77°) is first distilled off, and the sulphur monochloride (b.-p. 136°) is purified for use in vulcanizing rubber.

Carbon tetrachloride is a colorless liquid which dissolves fats, tars, and many other organic compounds. It is used to take the oil or grease out of wool, linen, oil-bearing seeds and bones. It has a great advantage over gasoline (petrol) and benzine (see p. 586), which can be used for similar purposes, in that it is non-inflammable. "Carbona," used for removing stains from clothing, gloves, and shoes, is benzine to which sufficient carbon tetrachloride has been added to render the mixture non-inflammable. "Pyrene" fire extinguishers contain, mainly, carbon tetrachloride. The temperature of the burning material is lowered, because heat is consumed in vaporizing the liquid and, at the same time, the vapor displaces the air and stops the combustion.

**Calcium Carbide  $\text{CaC}_2$  and Carborundum  $\text{SiC}$ .** — Calcium carbide is manufactured in an electric furnace (Thomas Willson, a Canadian) by the interaction of finely pulverized limestone or quicklime with coke:



The operation is a continuous one, the materials being thrown into the left side of the drum (Fig. 128, diagrammatic), and the product removed on the right. The carbon poles are fixed. The arc having been established, the drum is rotated slowly as the carbide accumulates. The current enters by one carbon, passes through the carbide, and leaves by the other. The high resistance of the partially transformed material causes the production of the heat. When the action in one layer approaches completion, the resistance falls, the current increases, and an armature round which the wire passes (not shown in Fig. 128) comes into operation and turns the drum. In this way the carbide just formed is continuously moved away from the carbons, and new material, introduced on the left, falls into the path of the current. The iron plates which

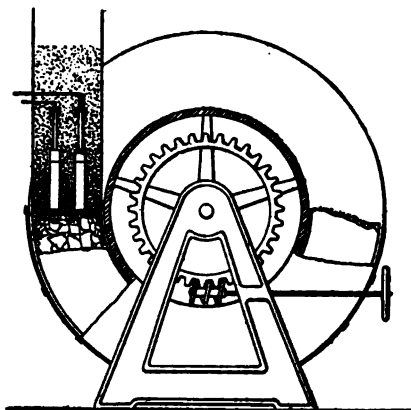
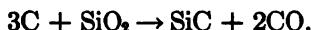


FIG. 128.

form the circumference of the drum are added on the left and removed on the right, where also the carbide is broken out with a chisel. The drum revolves once in about three days. The product is used for making acetylene (*q.v.*).

**Carborundum**, or carbide of silicon  $\text{SiC}$ , of which hundreds of tons are manufactured annually at Niagara Falls (Acheson's process), is made in an electric furnace of the type shown in Fig. 127 (p. 569). A mixture of coke and sand (silicon dioxide  $\text{SiO}_2$ ), containing some sawdust, is piled between the terminals, with a core of granular carbon to carry most of the current. The resistance produces a high temperature ( $1950^\circ$ ), and the sand is reduced:



The carborundum remains, often in beautifully crystalline form. It is exceedingly hard (Appendix II), and after pulverization and mixing with a filler, is molded into grinding wheels and whet-stones. Carborundum decomposes at  $2220^\circ$ . It is not affected by water or acids, but is decomposed by alkalies.

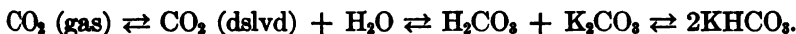
**The Oxides of Carbon.** — Four oxides of carbon are known, of which two, namely the dioxide  $\text{CO}_2$  and the monoxide  $\text{CO}$ , are familiar. Carbon suboxide  $\text{C}_3\text{O}_2$ , and mellitic anhydride  $\text{C}_{12}\text{O}_9$  (50 per cent carbon and 50 per cent oxygen) are best classed as organic compounds. Two other oxides,  $\text{C}_8\text{O}_6$  and  $\text{C}_6\text{O}_6$ , are known only in the hydrated forms, namely leuconic acid and triquinoyl, respectively.

### CARBON DIOXIDE AND CARBONIC ACID

**Occurrence.** — Carbon dioxide is present in the atmosphere, and issues from the ground in large quantities in certain neighborhoods, as, for example, near the Lake of Laach, in the so-called Valley of Death in Java, and in the Grotta del Cane near Naples. Effervescent mineral waters contain it in solution, and their effervescence is caused by the escape of the gas when the pressure is reduced. Well-known waters of this kind are those of Selters (whence, by a singular perversion, the English word *seltzer* is derived), of Vichy and of the Geyser Spring at Saratoga.

**Modes of Formation.** — 1. Carbon dioxide is produced by combustion of carbon with an *excess* of oxygen:  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ . The combustion of all compounds of carbon, as well as the slow oxida-

tion in the tissues of plants and animals, leads to the formation of the same substance. The product from burning carbon is naturally mixed with at least four times its volume of atmospheric nitrogen. To secure carbon dioxide for commercial purposes from this source, the gas is led under pressure into a solution of potassium carbonate, which absorbs the carbon dioxide:



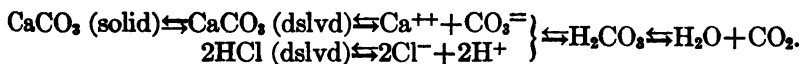
When the pressure is reduced by a pump, all the actions are reversed, and the gas escapes in pure form. The same solution, with occasional purification, can be used an indefinite number of times.

2. It was Joseph Black (1757) who first recognized the gas as a distinct substance. He observed its formation when marble or magnesium carbonate was heated:



and named the gas "fixed air" from the fact that it was contained in these solids. The above action had been used for centuries in making quicklime (calcium oxide). All common carbonates, excepting the normal carbonates of potassium and sodium, decompose in this way, leaving the oxide of the metal or the metal itself (p. 130).

3. Black found that the gas was also produced when acids acted upon carbonates, and this method is commonly employed in the laboratory:



Since the carbonic acid is very slightly ionized, the action is like that of acids on sulphites (p. 424). Since, however, the carbonate of calcium (marble) is very slightly soluble, so that an additional equilibrium controls its solution, the action is like that of acids on ferrous sulphide (p. 419). The apparatus shown in Fig. 41 (p. 119) is used.

4. Carbon dioxide is also a product of the fermentation of sugar (*q.v.*), as Black had the credit of showing. It is formed also, with the assistance of bacteria, in the decay of animal and vegetable matter (p. 91).

**Physical Properties.** — Carbon dioxide is a colorless, odorless gas. It is one-half heavier than air. The G.M.V. weighs 44.26 g. The critical temperature is 31.35°. The solid melts at -56°, having

a vapor pressure of 5.3 atmospheres. The solid has a vapor pressure of 1 atmos. at  $-79^{\circ}$ . The density of the liquid at  $0^{\circ}$  is 0.95. At  $0^{\circ}$  its vapor tension is 35.4 atmospheres and at  $20^{\circ}$  59 atmospheres. It must be preserved, therefore, in very strong cylinders of mild steel. Large quantities of it, often collected from fermentation vats, are sold in such cylinders, and used in operating beer-pumps and in making aerated waters. When the liquid is allowed to flow out into an open vessel or, better still, into a cloth bag (nonconductor of heat), it cools itself by its own evaporation and forms a white, snowlike mass. Solid carbon dioxide evaporates at  $-79^{\circ}$  without melting, since at that temperature it exercises 1 atmosphere pressure, and the heat from the surroundings is used as heat of vaporization instead of being employed in raising the temperature to the melting-point ( $-56^{\circ}$ ).

The solid is used in the laboratory as a cooling agent, being often mixed with ether to give closer contact with the vessel ( $-80^{\circ}$ ). Mercury (m.-p.  $-40^{\circ}$ ) is easily frozen by the mixture.

The great contrast in the speeds of a chemical change at two temperatures (*cf.* p. 93) may be illustrated by putting a minute piece of sodium in some 30 per cent hydrochloric acid which has been cooled in the above mixture. Hardly any interaction can be observed. But if the temperature of the acid is allowed to rise, the action becomes more and more rapid, and ends by being explosively violent.

Carbon dioxide gas (760 mm. and  $15^{\circ}$ ) dissolves in its own volume of water. Up to four or five atmospheres Henry's law (p. 188) describes its solubility accurately. An aqueous solution, prepared under a pressure of 8-10 atmospheres, is familiarly known as *soda water*, or carbonated water.

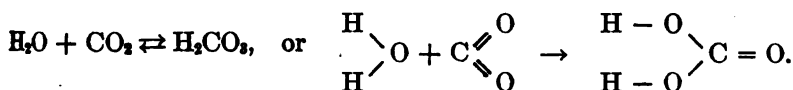
**Chemical Properties.**—Carbon dioxide is a stable compound. At  $2000^{\circ}$  (760 mm. press.) the dissociation reaches 1.8 per cent ( $2200^{\circ}$ , 4.9 per cent;  $2500^{\circ}$ , 15.8 per cent):  $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$ , or about the same as that of water.

The more active metals, like magnesium, burn brilliantly when ignited in a hollow lump of solid carbon dioxide, producing the oxide of the metal and free carbon. Less active metals, such as zinc and iron, when heated in a stream of the gas, give an oxide of the metal and carbon monoxide (*q.v.*).

Carbon dioxide unites directly with many oxides, particularly those of the more active metals, such as the oxides of potassium,

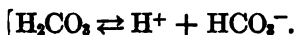
sodium, calcium, etc., giving the carbonates. Hence the decomposition of calcium carbonate by heating (p. 573) is a reversible action, which proceeds in the opposite direction when a sufficient pressure of carbon dioxide is used (*cf.* p. 153).

Carbon dioxide, when dissolved in water, forms an unstable acid:



The name carbonic acid is frequently, though improperly, given to the anhydride  $\text{CO}_2$ , which has no acid properties.

**Chemical Properties of Carbonic Acid  $\text{H}_2\text{CO}_3$ .** — The solution of carbon dioxide in water exhibits the properties of a weak acid. It conducts electricity, although not well. It turns litmus red, though not so decidedly as do strong acids. Its feebleness is due, however, not exclusively to the small degree of ionization, but also to the fact that ordinary solutions of carbon dioxide are necessarily very dilute. The ionization takes place chiefly according to the equation:



In a deci-normal solution, less than two molecules of the acid in a thousand are ionized. The conditions of equilibrium between the gas and the solution are precisely similar to those described under sulphurous acid (p. 444).

**Carbonates and Bicarbonates.** — When excess of an aqueous solution of carbonic acid is mixed with a solution of a base like sodium hydroxide, or, as the operation is more usually performed, when carbon dioxide is passed directly into a solution of the alkali, water is formed and the acid carbonate (**bicarbonate**) of sodium remains dissolved:



Although the bicarbonate is technically an acid salt, its solution is neutral on account of the exceedingly slight dissociation of the  $\text{HCO}_3^-$  ion. By addition of an equivalent of sodium hydroxide to the solution of the bicarbonate the normal carbonate is obtained:

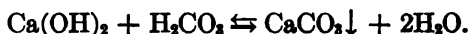


This solution, like that of all salts of a strong base and a feeble acid (*cf.* p. 399), is alkaline in reaction. This is because the tendency to form the very slightly ionized  $\text{HCO}_3^-$  makes the foregoing ionic action noticeably reversible (*cf.* pp. 419, 559).

The **normal carbonates**, with the exception of those of potassium, sodium, and ammonium, are insoluble in water, and may be obtained by precipitation when the proper ions are employed. For example:



The aqueous solution of carbon dioxide interacts with solutions of barium and calcium hydroxides in a similar manner:



These precipitations are used as **tests** for carbon dioxide and as a means of estimating its amount in a sample of air (p. 501).

Excess of carbon dioxide converts calcium carbonate into the more soluble bicarbonate, and hence considerable quantities of "lime" (hardness, *q.v.*) are frequently held in solution by natural waters, all of which contain carbon dioxide in solution:

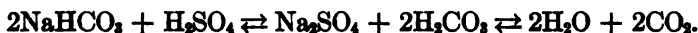


A considerable excess of carbon dioxide is required to convert the whole of the carbonate into the soluble bicarbonate, since the action is markedly reversible. In the same fashion, the carbonates of iron  $\text{FeCO}_3$  (chalybeate water), magnesium, and zinc are dissolved as bicarbonates in water containing free carbonic acid. In fact, the solution, transportation, and deposition of all these carbonates take place in nature on a large scale by the alternate progress and reversal of this action.

**Uses of Carbon Dioxide.**—The employment of the gas for impregnating aerated waters has been mentioned. The gas is used in immense quantities in the manufacture of sodium bicarbonate  $\text{NaHCO}_3$  (baking soda), of sodium carbonate  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  (washing soda), and of white lead, a basic carbonate of lead  $\text{Pb}_2(\text{OH})_2(\text{CO}_3)_2$ .

Since carbon dioxide is already fully oxidized, it does not burn, and since it is very stable, ordinary combustibles will not burn in it. A small percentage of it will destroy the power of air to support combustion. For this reason, portable **fire extinguishers** contain a dilute solution of sodium bicarbonate, and a bottle of

sulphuric acid. When the tank is inverted, the acid flows into the solution:

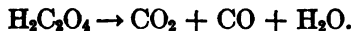


The liquid is saturated with the gas and the excess, rising to the top, by its pressure forces the solution out through the nozzle. The liquid is more effective than an equal amount of water, because the carbon dioxide it carries mixes with the surrounding air.

The most wonderful chemical change which carbon dioxide undergoes is perhaps the most useful to mankind, and at the same time the one least understood. This is the action by which *plants use it as food* (see p. 579).

### CARBON MONOXIDE CO

**Preparation.**—In the laboratory, carbon monoxide may be obtained by heating oxalic acid, a solid, white, crystalline substance, in a flask with concentrated sulphuric acid. The latter is here employed simply as a dehydrating agent (p. 438):



To obtain pure carbon monoxide from this mixture, it is necessary to remove the carbon dioxide, by passing the gas through a solution of potassium hydroxide contained in a wash bottle. By using formic acid, or sodium formate, with sulphuric acid, the presence of the carbon dioxide is avoided:  $\text{HCHO}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ .

We commonly observe the blue flame of burning carbon monoxide playing on the surface of a coal fire. The gas is produced by the passage of the carbon dioxide, which is first formed, through the upper layers of heated coal:  $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$ . A similar reduction of carbon dioxide is produced when the gas is led over a metal, such as zinc, and heat is applied:  $\text{CO}_2 + \text{Zn} \rightarrow \text{ZnO} + \text{CO}$ .

**Producer Gas and Water Gas.**—When coke and air are used in the reaction mentioned above, the mixture of carbon monoxide (about 33 per cent) and nitrogen (about 66 per cent) obtained is called **producer gas**. It is combustible and is used in factories for heating and to drive gas engines for power.

When steam is driven through white hot coke or anthracite, a mixture of hydrogen and carbon monoxide, known as **water gas** is produced:





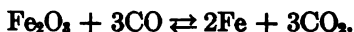
The coke, piled in a brick-lined, cylindrical structure, is brought to vigorous combustion by blowing in air for ten minutes. The steam is substituted for the air. Since the interaction takes place with absorption of heat (is endothermal, see equation), in about five minutes the coke becomes too cool. Air is then substituted for steam, and so on alternately. The gas is collected while the steam is turned on, and contains equal volumes of the two gases together with some carbon dioxide (4-7 per cent), nitrogen (4 per cent) and oxygen (1 per cent). The gas is, therefore, almost wholly combustible and is used as a source of heat, and for driving gas engines to furnish power. It is used also for making illuminating gas (*q.v.*). Since carbon monoxide is more easily liquefied than is hydrogen, the latter gas is obtained, for commercial use, by passing water gas through a liquefier.

When both steam and air are driven *together* over burning coke the latter is able to burn continuously, and a fuel gas which is a cross between producer gas and water gas is obtained.

Fuel gases are used on a large scale in steel works, and other factories. They give a uniform and easily regulated heat, they leave no ash, and their use involves no labor for stoking. As gases also, they can be used in structures in which coal, as a solid, could not be employed.

**Physical Properties.**—Carbon monoxide is a colorless gas with a metallic taste and odor (poisonous!). It is very slightly soluble in water. Its density is almost the same as that of air, for the G.M.V. weighs 28 g. When liquefied it boils at  $-190^{\circ}$ .

**Chemical Properties.**—All the chemical properties of carbon monoxide are referable to the fact that in it the element carbon is bivalent:  $C = O$ . The compound is in fact **unsaturated**, and combines with oxygen, chlorine, and other substances directly. Thus the gas burns in the air, uniting with oxygen to form carbon dioxide. Again, iron (*q.v.*) is manufactured by the reduction of the oxide of iron by gaseous carbon monoxide in the blast furnace:



In sunlight carbon monoxide unites directly with chlorine to form carbonyl chloride  $COCl_2$ . It is absorbed by a solution of cuprous chloride in hydrochloric acid, forming a compound said to be  $CuCOCl, H_2O$ . It unites directly with certain metals, notably

nickel and iron, with which it forms the so-called nickel carbonyl  $\text{Ni}(\text{CO})_4$  (*q.v.*) and iron carbonyl, respectively. The gas reduces Fehling's solution (*q.v.*), and precipitates silver from ammonio-silver nitrate solution.

The gas is an active poison. When inhaled it unites with the hæmoglobin of the blood, to the exclusion of the oxygen which forms with the hæmoglobin a less stable compound (*cf.* p. 92). A quantity equivalent to about 10 c.c. of the gas per kilo. weight of the animal is sufficient to produce death, about one-third of the whole hæmoglobin having entered permanently into combination with carbon monoxide. One volume in 800 volumes of air produces death in about thirty minutes. This gas is the chief poisonous substance in illuminating gas. The poisonous effect of tobacco smoke, when inhaled, is partly due to the carbon monoxide produced by incomplete combustion. Nicotine, although contained in tobacco leaves, is unstable, and is decomposed by the heat. Traces of other irritant organic compounds, however, are contained in the smoke.

The quantities of heat given out by the successive unions of two units of oxygen with one unit of amorphous carbon are worth recording:



It will be seen that the addition of the second atom of oxygen appears to cause the evolution of a very much larger amount of heat than does that of the first. It must be remembered, however, that the carbon monoxide is gaseous, while the carbon in the first equation is solid. The heats produced by the unions of the two units are probably not very different, but in the first case a large amount of the heat is used up in bringing the carbon into the gaseous condition.

**Carbon Suboxide  $\text{C}_3\text{O}_2$ .** — This oxide is obtained by the action of phosphorus pentoxide (dehydrant) on malonic acid.  $\text{H}_2(\text{CO}_2)_2\text{CH}_2 \rightarrow 2\text{H}_2\text{O} + \text{C}_3\text{O}_2 \uparrow$ . It is a colorless liquid, boiling at  $7^\circ$ . The vapor has an unpleasant odor. With water it gives malonic acid, of which it is the anhydride. If kept for a day, it changes into a dark red solid of the same composition.

**Carbon Dioxide as Plant Food.** — The walls of the cells which form the framework of a plant are made of cellulose  $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ . In the cells, especially those in certain parts of the plant, granules of starch  $(\text{C}_6\text{H}_{10}\text{O}_5)_y$  are found, and in the fruit, sugars  $\text{C}_6\text{H}_{12}\text{O}_6$  or  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  are stored. The plant contains also proteins. These sub-

stances contain carbon, hydrogen, oxygen, nitrogen, sulphur, and phosphorus, and plant food must furnish these elements. Compounds of potassium are also required. Hence, in addition to large amounts of water ascending through the roots and stem, carrying sufficient quantities of soluble compounds of the four elements last named, all plants require an abundant supply of carbon in absorbable form. Now, this comes from atmospheric carbon dioxide, admitted through minute openings (stomata) situated mainly on the lower surfaces of the leaves. Comparison of the formulæ  $\text{CO}_2$  and  $\text{C}_6\text{H}_{10}\text{O}_5$ , shows at once that the assimilation of the carbon dioxide of the plant must involve *reduction*. The chlorophyll (green matter) and protoplasm in the leaves act upon the carbon dioxide, causing oxygen gas to be liberated. It is believed that the carbon dioxide is reduced to formaldehyde  $\text{CH}_2\text{O}$ , and from this sugars can be made in the laboratory:  $6\text{CH}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6$ . It is supposed that the various chemical compounds which plants construct in large quantities, such as sugar, starch, and cellulose, are built up as the result of actions like this. In a rough fashion, and disregarding the steps by which the process takes place, we may represent the chemical change by means of the thermochemical equation:



These figures indicate roughly (p. 35) the amount of energy stored for cellulose, and the values for the other compounds are of the same order. This action goes on only in sunlight (see next section) and if green leaves are placed under water saturated with carbon dioxide, oxygen is given off and can be collected.

The enormous amount of energy absorbed in the action, and represented in terms of heat in the equation, is furnished by the sunlight. It may be added that plants, like animals, also use some oxygen and produce some carbon dioxide, but this process is entirely overborne in daylight, and is noticeable only in the dark.

The energy that does the world's work comes mainly from two sources, namely, water power and the combustion of wood or coal (which is fossil wood). The water comes from vapor, generated by the *sun's heat*, condensed as rain, and ultimately feeding the rivers. The source of the energy in wood and coal is now apparent. When wood, which is largely cellulose  $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ , burns, it gives carbon dioxide, water, and heat. In fact, its combustion is represented by the above equation, *when read backwards*. Thus, the sunlight, through the machinery of the plant, takes carbon dioxide

and water, supplies the energy (as light), and gives us wood and oxygen. And the wood and oxygen, when burned, give us back the original substances, and the equivalent of the original energy in the form of heat. Thus, the two sources of energy turn out to be the same, namely the sun's rays.

If, instead of burning the starch of the plant, we consume it as food, it goes through *several* changes instead of one. But the final products are the same, namely carbon dioxide and moisture, given off through our lungs and skin, and heat and other forms of energy such as are developed in animals. Thus, whether we use our muscles, a steam engine, or a water turbine to do work, sunlight is in each case the ultimate source of the energy employed.

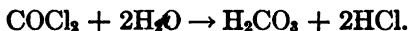
It should be noted that the energy is not stored exclusively in the coal, but is shared between coal and the oxygen of the air. If our atmosphere consisted of compounds of carbon, then the material corresponding to stores of coal would have to be oxygen or compounds of oxygen, and we should be likely then to speak of the energy as being stored for us and sold in the form of oxygen. That we are in the habit of speaking of it, at present, as going with the carbon is because the oxygen of the air is supplied free of charge, while the coal and wood have to be purchased.

**Photochemical Action.** — We have seen that light may simply act catalytically, as on a mixture of hydrogen and chlorine (p. 222) or an aqueous solution of hypochlorous acid (p. 474). These actions involve the liberation of energy and go on spontaneously (*cf.* p. 35) under proper conditions. On the other hand, light may actually be consumed in large amount in producing a chemical change, as in decomposing silver chloride (p. 19), or in the above instance. All wave lengths of light, which is the same as to say all colors of light, are not equally active in any one case. **But there is no particular set of wave lengths which is of special chemical activity.** In the action on silver chloride, green and blue light is very active, while red is almost without effect. Here, in the actions in which chlorophyll is concerned, it is the red and yellow light that produces the chemical change, and a plant exposed to blue light (*e.g.*, by shading with blue glass) will assimilate none of the carbon dioxide in the air surrounding it. The chemical substances in the retina of the eye seem to resemble those in the leaves of plants, for they are most affected by red and yellow light. To put this another way, a spectrum of uniform intensity throughout, when viewed by a plant or a human eye, would appear to be brightest in the red and yellow portions, while a con-

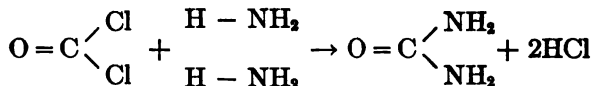
siderable stretch towards the blue extremity would actually be invisible. On the other hand, to an eye in which the active substance was silver chloride, if such an eye could be imagined as existing, the red end would be invisible and the blue and ultra-violet would be the most brilliant parts.

### CARBONYL CHLORIDE AND UREA

**Carbonyl Chloride  $\text{COCl}_2$ .**— This substance is also named **phosgene** (Gk.  $\phi\acute{o}s$ , light;  $\gamma\acute{\epsilon}\nu\eta\acute{\alpha}\nu$ , to produce), on account of its formation by the catalytic influence of sunlight (p. 581). On a commercial scale it is obtained by passing the mixed carbon monoxide and chlorine over animal charcoal (contact agent). It is a liquid which boils at  $8^\circ$ , possesses a suffocating odor, and is very soluble in benzene and some other hydrocarbons. When brought into contact with water it is hydrolyzed at once, forming carbonic acid and hydrochloric acid:



**Urea.**— When ammonia and carbonyl chloride are mixed in the proper proportions, in solution in toluene, urea, a most interesting chemical substance, is produced:



Excess of ammonia has to be used to combine with the hydrogen chloride thus set free, so that the final equation is:



The urea, a white, crystalline solid, is soluble in alcohol, while ammonium chloride is not, so that the former may be washed out by means of this solvent and recovered by evaporation. A little reflection will show that, using the above action as the final stage, urea can be built up from the simple substances composing it.

Urea was known long before any method for its synthesis had been discovered. It is the chief product of the decomposition of compounds of nitrogen in the animal body, and is found in the liquid excrements of animals. It was regarded as a typical organic substance, in the old sense of the word (p. 566). In 1828, Wöhler succeeded in preparing it artificially (see below). This was the first synthesis by a chemist of a true "organic" substance, and its prepara-

tion proved to be the precursor of many discoveries of a similar nature. From a later year, about 1840, we may date the transition of organic chemistry, a science in which the mystery of life was supposed to be supreme, into the chemistry of the compounds of carbon, which is a branch of inorganic chemistry.

Wöhler used ammonium cyanate (*q.v.*), a substance in whose preparation we are independent of all products of life processes. When ammonium cyanate, or a mixture of any ammonium salt with potassium cyanate in solution in water, is warmed for some time, an intramolecular change (*cf.* p. 20) takes place, and long prisms of urea are deposited as the liquid cools:



Since the action is reversible, about four or five per cent of the ammonium cyanate remains unchanged.

The two substances just mentioned are entirely different in chemical properties. Ammonium cyanate is a highly ionized salt, while urea is not a salt at all, but a substance like ammonia which unites with acids to form salts. Materials which, like these, have the same composition and the same numbers of units in their molecules, and yet possess different properties, are spoken of in chemistry as *isomers*. The formulæ we have employed attempt to explain the differences in their properties by suggesting a difference in their molecular structure (*cf.* p. 442).

Assisted by the catalytic action of certain ferments, urea, when dissolved in water, can take up two molecules of the solvent to form ammonium carbonate:



Ammonium carbonate (*q.v.*) is an unstable compound, and in turn, gives off ammonia and carbon dioxide. To this action is due in part the strong odor of ammonia arising from the decomposition of sewage.

**Exercises.** — 1. To which of the factors in the interaction of calcium carbonate and hydrochloric acid (p. 573) is due the forward displacement of all the equilibria?

2. What will be the excess of pressure inside a bottle of soda-water when four volumes of carbon dioxide are dissolved in one volume of water?

3. What volume of liquid carbon dioxide, measured at 0°, will be required to give 75 liters of the gas at 0° and 760 mm. pressure?

4. What will be the effect of increase in pressure on the dissociation of carbon dioxide (p. 574)?

5. Prepare a diagram showing the whole scheme of equilibria involved in the hydrolysis of sodium carbonate (p. 576).
6. What volume of carbon dioxide at  $0^{\circ}$  and 760 mm. is required for complete interaction with one liter of normal sodium hydroxide?
7. What are the exact relative weights of equal volumes of carbon dioxide, carbon monoxide, air, and steam?

## CHAPTER XXIX

### THE HYDROCARBONS. ILLUMINANTS. FLAME

THE compounds of carbon and hydrogen are called the **hydrocarbons**. Petroleum is a mixture of many substances of this class. The hydrocarbons are, therefore, of great importance in connection with fuel, illumination, and lubrication.

#### THE HYDROCARBONS

More than two hundred and fifty compounds of carbon and hydrogen have been described. They fall into several distinct series, the chief one of which contains methane  $\text{CH}_4$  as its simplest member. On account of the fact that certain members of this set are found in paraffin, it is commonly known as the **paraffin series**. For the reason that in this series the carbon has all its four valences employed, the members are also called the **saturated hydrocarbons**.

**Paraffin or Saturated Series of Hydrocarbons.** — The following list gives the formulæ of a few members of this series, with their names, and the boiling-points of seven of the simplest hydrocarbons, and of two of the higher members of this series:

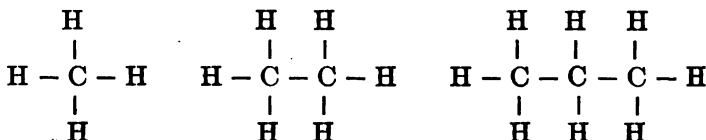
Methane	$\text{CH}_4$	b.-p. $-164^\circ$	Hexane	$\text{C}_6\text{H}_{14}$	b.-p. $71^\circ$
Ethane	$\text{C}_2\text{H}_6$	" $-89.5^\circ$	Heptane	$\text{C}_7\text{H}_{16}$	" $99^\circ$
Propane	$\text{C}_3\text{H}_8$	" $-37^\circ$	Hexadecane	$\text{C}_{16}\text{H}_{34}$	" $287.5^\circ$
Butane	$\text{C}_4\text{H}_{10}$	" $+1^\circ$	"	"	m.-p. $18^\circ$
Pentane	$\text{C}_5\text{H}_{12}$	" $35^\circ$	Pentatricontane	$\text{C}_{30}\text{H}_{62}$	" $74.7^\circ$

After the first four, the names are based on the Greek numerals representing the number of carbon atoms in the molecule. Heptane is followed by octane  $\text{C}_8\text{H}_{18}$ , nonane  $\text{C}_9\text{H}_{20}$ , decane  $\text{C}_{10}\text{H}_{22}$ , etc. On examining the formulæ, we perceive that, in each, the number of hydrogen atoms is equal to twice the number of carbon atoms plus two. The general formula is therefore  $\text{C}_n\text{H}_{2n+2}$ . Substances related in this way form an **homologous series**. The series illustrates strikingly the law of combining weights (p. 61). We



note, also, that the **first four are gases** at room temperature. The members from pentane to pentadecane  $C_{15}H_{32}$  are **liquids**, and from hexadecane onward they are **solids**.

In these compounds the carbon is quadrivalent, and each substance is related to the preceding one by containing the additional unit  $CH_2$ . The graphic formulæ of the first three members illustrate these two facts:



Transferences of H one step to the right and interpositions of  $CH_2$  constitute the successive differences.

**Petroleum.** — Petroleum is a thick, often greenish-brown colored oil. When borings reach the oil-bearing strata, the oil, hitherto held beneath impervious strata, and often under hydrostatic pressure of water underneath or around it, either gushes up or is pumped to the surface. Wells are in operation in Caucasia, Galicia, India, Japan, and in Ontario, Ohio, Pennsylvania, California, Oklahoma, and elsewhere. The world's production in 1912 was 400 million barrels (42 gal. each), of which 266 millions were produced in the United States. In oil-refining, advantage is taken of the differences in the boiling-points to make a partial separation of the components by fractional distillation (see below). The compounds containing sulphur which are often present, and would give the obnoxious sulphur dioxide when the oil was burned, are deprived of this constituent by heating the oil with powdered cupric oxide (Frasch process). The unsaturated hydrocarbons (*q.v.*) are removed by agitation with concentrated sulphuric acid. The following are some of the products of the oil refinery, with their components and uses.

Name.	Components.	B.-P.	Uses.
Petroleum ether .	Pentane-hexane	40°- 70°	Solvent, gas-making
Gasoline (petrol) .	Hexane-heptane	70°- 90°	" fuel
Naphtha . . . . .	Heptane-octane	80°-120°	" "
Benzine . . . . .	Octane-nonane	120°-150°	" "
Kerosene . . . . .	Decane-hexadecane	150°-300°	Illuminating-oil

The portions of still higher boiling-point are used as lubricating oils, and the residue for fuel. Special treatment, such as super-heating the vapor under high pressure (Rittman's process), is used to increase the proportion of **gasoline** (petrol) for which there is a large and increasing demand.

The vapor of these products is more inflammable the more volatile the components. The sale of kerosene is controlled legally by the requirement that the vapor it gives when heated shall not catch fire from a naked flame until the oil has reached a certain minimum temperature, the "flash-point." This varies from  $37.7^{\circ}$  to  $68.5^{\circ}$  in different states and countries. To be used safely, the flash-point should be  $65^{\circ}$  ( $150^{\circ}$  F).

At some suitable stage, the residual oil is chilled, and a quantity of the solid members of the series ( $C_{22}H_{46}$  to  $C_{28}H_{58}$ ) crystallizes in flakes (solid **paraffin**) and is separated by filtration in presses. The paraffin is used in waterproofing paper, in laundry work, and as an ingredient in candles. In some cases **petrolatum** (vaseline), consisting of substances melting at  $40^{\circ}$ – $50^{\circ}$ ,  $C_{22}H_{46}$  to  $C_{28}H_{58}$ , is obtained also.

From **ozocerite**, which is a sort of natural paraffin, ceresin, a substitute for beeswax, is made. **Asphalt** is another natural mixture of solid hydrocarbons, found particularly in Trinidad, and used in road-making.

The formation of these hydrocarbons in nature is not yet thoroughly explained. According to one theory, they are formed by the action of water upon carbides of metals; while according to another, they result from the decomposition of vegetable or animal matter. Possibly both of these sources have contributed to their formation. Certain differences between the natural oils of different localities, such as the presence of aromatic hydrocarbons in California, point, at all events, to some difference in their origin or subsequent treatment.

**Fractional Distillation.** — When the boiling-points of two components of a liquid are very far apart, the vapor pressure of the one may be very low, when that of the other, by heating, has reached 760 mm. In this case the first distillate will contain little of the high-boiling component. When, as in the case of petroleum, the differences in boiling-points are not great, complete separation of the components is difficult. Yet by distillation in which the distillate is caught, not in one vessel, but in several successwely, "fractions"

are obtained such that the earlier ones contain more of the low-boiling and the later ones more of the high-boiling materials. The distillate is diverted into different vessels when the thermometer immersed in the vapor (Fig. 20, p. 43) reaches certain temperatures, or (in petroleum refineries) when the density of the distillate reaches certain values, so that fractions of the same kind are kept together. When these fractions are then distilled one at a time, beginning with the lowest, and the several distillates are divided from one another by the same temperatures as before, a more complete separation is effected. This process is called **fractional distillation**, and may be repeated as often as we please with constantly increasing differentiation of the fractions.

An experimental illustration may be given by mixing 0.4 c.c. of benzene (b.-p. 80.4°) with 8 c.c. formic acid (b.-p. 100°) and 2 c.c. benzyl alcohol (b.-p. 206.5°), and boiling a part of the mixture in a test-tube with a small flame. The components come off in succession, and are recognized by the fact that the first and last burn with a luminous flame, while the flame of the second is non-luminous [Lect. exp.]. By passing the vapors into a condenser, and using the method described above, a more or less complete separation can be made.

**General Properties of Paraffins.** — All these substances are extremely indifferent in their chemical behavior. They have none of the properties of acids, bases, or salts. The halogens, notably chlorine and bromine, however, interact with them (see below). When burned they all produce carbon dioxide and water. When their vapors are passed through a white-hot tube they suffer decomposition into a mixture of hydrogen and hydrocarbons of smaller or larger (see Benzene) molecular weight.

**Methane  $CH_4$ .** — Methane, otherwise known as **marsh-gas**, is the chief component of **natural gas**. It rises to the surface when the bottoms of marshy pools are disturbed, and issues from seams in coal beds. In these two cases it results from the decomposition of vegetable matter in absence of air. When methane enters mines from a coal seam it is called "fire-damp" (Ger. *Dampf*, vapor), on account of the explosive nature of the mixture it forms with the air. The carbon dioxide formed by the explosion is called by the miners "choke-damp." In many regions it is confined, like the oil, beneath impervious strata and is forced out through borings by hydro-

static pressure. It is found mainly in or near the localities where oil is found.

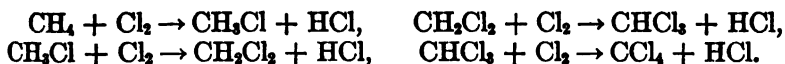
The *formation* of methane by direct union of carbon and hydrogen has already been discussed (p. 570). It may be made from inorganic materials by the action of water upon aluminium carbide, prepared by the interaction of aluminium oxide and carbon in the electric furnace (*cf.* p. 569):



In the *laboratory* the gas is commonly obtained by the distillation of a dry mixture of sodium acetate and sodium hydroxide:



As regards **chemical properties**, methane, like other saturated hydrocarbons (p. 588), is very indifferent. When a mixture of methane and chlorine is exposed to sunlight several changes occur in succession (*cf.* p. 225):



This kind of interaction with the halogens is characteristic of the saturated hydrocarbons. It takes place slowly, and is therefore entirely different from ionic chemical change. It consists in a **progressive substitution** of chlorine for hydrogen, unit by unit. The various groups which, in the first three of these products, are associated with chlorine, occur in many organic compounds, and receive the names methyl  $\text{CH}_3-$ , methylene  $\text{CH}_2=$ , and methenyl  $\text{CH}\equiv$ . The compounds are known, therefore, as methyl chloride, methylene chloride, methenyl chloride (**chloroform**), and carbon tetrachloride (p. 570). The last two are volatile liquids, and familiar substances. The corresponding iodine derivative **iodoform**  $\text{CHI}_3$  is used in surgical dressing. These substances are not salts, and are not ionized in solution. They are very slowly hydrolyzed by water—carbon tetrachloride, for example, giving carbonic acid and hydrochloric acid. Although carbon is a non-metal (*cf.* p. 209), this action requires a high temperature. Methane and the other saturated hydrocarbons are decomposed by strong heating (see cracking, below).

**Organic Radicals.**—In carbon chemistry there are groups of units which pass unaltered from compound to compound and receive the name **organic radicals**. They usually lack a property which inor-

ganic radicals generally possess, namely, the power to form ions (p. 324). Methyl is such a radical, being found in methane  $\text{CH}_3\text{H}$ , methyl chloride  $\text{CH}_3\text{Cl}$ , methyl alcohol  $\text{CH}_3\text{OH}$ , and acetic acid  $\text{CH}_3\text{CO}_2\text{H}$ . Similarly we have ethyl  $\text{C}_2\text{H}_5$  in ethane  $\text{C}_2\text{H}_6$  and in ethyl alcohol  $\text{C}_2\text{H}_5\text{OH}$ . Methyl, ethyl, and propyl  $\text{C}_3\text{H}_7$ — are univalent radicals. We have also ethylene  $\text{C}_2\text{H}_4$ —, propylene  $\text{C}_3\text{H}_6$ —, and so forth, which are bivalent. Groups like  $\text{NO}_2^{\cdot}$  (p. 527),  $\text{NH}_2^{\cdot}$  (p. 519),  $\text{CH}_3\text{CO}^{\cdot}$ , and many more, are other non-ionizable radicals found in organic compounds (see Acetic acid, below).

**Unsaturated Hydrocarbons.**— In addition to the saturated series of hydrocarbons, several other series are known in which smaller proportions of hydrogen are present. Thus, **ethylene**  $\text{C}_2\text{H}_4$ , to which illuminating gas largely owes the luminosity of its flame, belongs to a series  $\text{C}_n\text{H}_{2n}$ , all the members of which contain two atoms of hydrogen less than the corresponding compounds of the first series. Again, **acetylene**  $\text{C}_2\text{H}_2$  is the first member of a series  $\text{C}_n\text{H}_{2n-2}$ , and **benzene**  $\text{C}_6\text{H}_6$  begins a series  $\text{C}_n\text{H}_{2n-6}$ , of which **toluene**  $\text{C}_7\text{H}_8$  (p. 527) is the second member.\* These are all unsaturated because the full valence of the carbon is not in use, and these compounds, therefore, unite more or less readily with hydrogen, chlorine, bromine, and concentrated sulphuric acid. The hydrocarbons of all the series are mutually soluble, but none of them dissolves in water.

Members of the ethylene and acetylene series are found in petroleum, and are formed also to some extent by decomposition during the distillation. As oil containing them acquires dark-colored products by chemical change, the oils are always refined before being sold. They are agitated with concentrated sulphuric acid, which unites with the unsaturated substances and, being insoluble in the oil, collects in a layer below it. The oil is finally washed free from the acid with dilute alkali and with water.

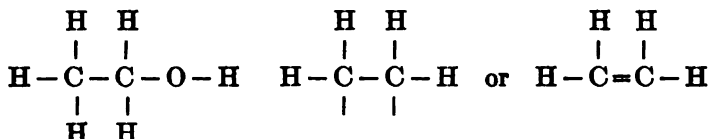
**Ethylene  $\text{C}_2\text{H}_4$ .**— Ethylene is the first member of the second series of hydrocarbons. It corresponds to ethane  $\text{C}_2\text{H}_6$ , but contains in each molecule two hydrogen units less than does this substance.

\* Isoprene  $\text{C}_5\text{H}_8$ , a member of the unsaturated series  $\text{C}_n\text{H}_{2n-4}$ , when heated in presence of sodium (or some other contact agent), changes into caoutchouc  $(\text{C}_5\text{H}_8)_x$  or raw rubber. No method of preparing artificial rubber has yet been used commercially.

Ethylene is **made** by heating common alcohol (ethyl alcohol) with concentrated sulphuric acid:



The action with sulphuric acid really takes place in two distinct stages, and the intermediate product can be isolated. First, ethyl hydrogen sulphate (*cf.* p. 385) is formed,  $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{C}_2\text{H}_5\text{HSO}_4 + \text{H}_2\text{O}$ . Above  $150^\circ$ , however, this substance, which is a thick syrup, is dissociated, giving ethylene and sulphuric acid,  $\text{C}_2\text{H}_5\text{HSO}_4 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{SO}_4$ . A comparison of the structural formulæ of the alcohol and ethylene shows that this loss of water must leave the carbon partly unsaturated:



The water may also be removed by allowing alcohol to fall drop by drop on heated phosphoric anhydride. The solid metaphosphoric acid remains behind and ethylene escapes.

Ethylene is formed along with acetylene and other substances, when any saturated hydrocarbon is heated strongly. Even methane gives it:



Ethylene is a gas, which, when liquefied, boils at  $-105^\circ$ . Its critical temperature is  $35^\circ$ . At  $0^\circ$  it may be liquefied by a pressure of 42 atmospheres. It burns in the air with a flame which, on account of the great separation of free carbon which takes place temporarily during the combustion (*cf.* Flame), is highly luminous. It will be seen that in the formula but three of the valences of each carbon unit are occupied. As carbon is usually either bivalent or quadrivalent, we should expect that in this compound the combining capacity of the carbon would not be completely satisfied. We find this to be the case. Ethylene is easily reduced by active hydrogen (p. 543) to ethane, taking up two units of hydrogen in the process. When ethylene is passed through liquid bromine, it is rapidly absorbed, and the bromine seems to increase in volume and finally loses all its color, leaving a transparent liquid having the composition  $\text{C}_2\text{H}_4\text{Br}_2$ , **ethylene bromide**. The second of the above graphic formulæ for ethylene

is the one generally used. In spite of appearances, it is not intended to indicate that the two units of carbon are more forcibly held together than in other compounds (*cf.* p. 138). It simply chronicles the fact that one valence of each carbon unit is unoccupied.

**Acetylene.** — This substance, likewise a gas, is the first member of still another unsaturated, homologous series,  $C_nH_{2n-2}$ . Its formula  $C_2H_2$  shows that its molecule lacks four of the hydrogen units necessary to the complete saturation which we find in ethane. Graphically its structure is usually represented thus:  $H - C \equiv C - H$ . This gas is formed in small quantities by direct union of carbon and hydrogen in the electric arc (p. 570). It is formed, not because the elements prefer to give this one of the many hydrocarbons, but because, at  $2000^\circ$  or over, the other hydrocarbons are decomposed, and acetylene is one in the formation of which the greatest amount of heat is absorbed (van't Hoff's law, p. 305, and see below). For the same reason, it is produced when ethylene is passed through a heated tube:  $C_2H_4 \rightarrow C_2H_2 + H_2$  (*cf.* Flame).

When calcium carbide (p. 571) is thrown into water, violent effervescence occurs, the carbide is disintegrated, a precipitate of calcium hydroxide is formed, and acetylene passes off as a gas:



This hydrolytic action is like that of water on calcium phosphide (p. 553), calcium sulphide (p. 421), and magnesium nitride (p. 514).

Acetylene burns with a flame which is still more luminous than that of ethylene. Its most characteristic property is that when passed through an ammoniacal solution of a cuprous salt, it yields a red precipitate of a carbide of copper known as **copper acetylide**. The equation:  $Cu_2(OH)_2 + C_2H_2 \rightarrow Cu_2C_2 + 2H_2O$ , partially represents the change. This red precipitate, when dried, is extremely explosive, on account of the great amount of energy set free when it breaks up into its constituents. Its formation is used as a test for acetylene in mixtures of gases.

Acetylene may be handled safely as a gas at the ordinary pressure, but, when contained in cylinders at more than two atmospheres pressure, it is readily exploded by any shock. This is due to the fact that it is an endothermal compound:  $C_2H_2 \rightarrow 2C + H_2 + 53,200$  cal. It is frequently made in generators, as needed, from calcium carbide, and is used for lighting on automobiles and in regions remote from a public supply of illuminating-gas. The acetylene tanks, which

are also in use, contain acetylene dissolved under high pressure in acetone, a form in which it can be handled safely.

When acetylene  $C_2H_2$  is burned, we obtain from  $2 \times 12 + 2 = 26$  g. not only the heat due to the combustion of the carbon ( $2 \times 12 \times 8040$  cal., p. 567), and of the hydrogen ( $2 \times 28,800$  cal.), but also the heat due to the decomposition of the gas (53,200 cal.). The temperature of the flame is therefore extraordinarily high. The oxyacetylene flame, produced by means of a suitable burner (Fig. 51, p. 126), is now used, under the name of the **acetylene torch**, for cutting metals. The gases are contained in portable tanks. Such a flame will melt its way through a 6-inch shaft of steel plate several feet wide in less than a minute, cutting the object in two. Steel buildings have thus been taken down, and ships (like the *Maine*) have been cut up for removal. Other gases, like blau gas and oil gas, made by cracking petroleum (see below), are now displacing acetylene for this purpose, as they are almost as effective, and the flame is more easily controlled.

The unsaturated nature of this substance is shown by the avidity with which it unites with hydrogen and the halogens, forming saturated compounds.

**Benzene  $C_6H_6$ .**—Limits of space forbid the discussion of any of the other series of hydrocarbons. One of the most important has not been mentioned, however. It is that of which the first member is **benzene**,  $C_6H_6$ . More than half of the known compounds of carbon are derived from this substance. Phenol (*cf.* p. 527)  $C_6H_5OH$  is the fundamental alcohol of this set. Benzene is obtained from the products of the dry distillation of coal (*cf.* Coal gas), being formed, probably, from the acetylene which the decomposition of other hydrocarbons yields. At all events, when acetylene is passed through a heated tube some benzene is produced,  $3C_2H_2 \rightarrow C_6H_6$ , along with free carbon and hydrogen. Toluene (p. 527)  $C_6H_5CH_3$  is the second member of this series.

**Cracking of Hydrocarbons.**—All hydrocarbons, when heated strongly (air-excluded) decompose or **crack**. The changes seem to be reversible, and the result therefore depends upon the conditions. Thus, at atmospheric pressure, and especially when the oil is mainly present as a liquid, hydrogen is given off and unsaturated liquid and gaseous hydrocarbons are produced. Under such conditions, ethylene is formed in large amounts. On the



other hand, when an oil free from gasoline is completely vaporized (500°), and is under high pressure, the hydrogen is forced into combination with the broken molecules and the saturated constituents of gasoline are produced in large amount (Rittman's process).

At a white heat, all the hydrocarbons decompose into hydrogen and free carbon. The latter is deposited in a dense form called **gas-carbon**, which is more or less crystalline (like graphite) and used in making carbon rods for arc lights and electric furnaces, and carbon plates for batteries, and for the electrodes employed in electrolysis. The carbon is ground up, moistened with petroleum residues, subjected to hydraulic pressure and finally heated strongly to expel volatile matter.

**Carburetted Water Gas.**—As we have seen, water gas is essentially  $H_2 + CO$  (p. 577), and burns with a pale-blue flame. To fit it for use as illuminating-gas, unsaturated hydrocarbons, which burn with a luminous flame, such as ethylene  $C_2H_4$  and acetylene  $C_2H_2$  must be added. The gas is sent through a tower containing strongly heated brick on which a petroleum oil is sprayed. Mixed with the vapor, the gas then passes into the "superheater" where, at a higher temperature, the cracking into unsaturated hydrocarbons occurs. The gas is then cooled and washed to remove condensible hydrocarbons, which would otherwise obstruct the service pipes. A typical carburetted water gas has the composition: Illuminants 17 per cent; heating gases, methane 20 per cent, hydrogen 32 per cent, carbon monoxide 26 per cent; impurities (nitrogen and carbon dioxide) 5–6 per cent. A flame burning 5 cu. ft. per hour gives 25 candle power.

**Blau gas** and **Oil gas**, such as Pintsch gas, contain larger proportions of illuminants. Thus a good gas shows: illuminants 45 per cent; heating gases, methane 39 per cent, hydrogen 14.5 per cent; impurities 1.5 per cent; candle power 65. Such gases are compressed in tanks and used for illumination on railway trains (Coal gas, see p. 612).

## FLAME

**Meaning of the Term.**—In the combustion of charcoal there is hardly any flame, for the light emanates almost entirely from the incandescent, massive solid. When two gases are mixed and set on

fire, a sort of flame passes through the mixture, but this can hardly be accounted a flame, in the ordinary sense, either. The rapid movement of the flash, and the explosion which accompanies it, are in a manner the precise opposite of the quiet combustion which is characteristic of flames.



Fig. 129.

With illuminating-gas the production of its very characteristic flame is due to the chemical union of a stream of one kind of gas in an atmosphere of another. The flame is made up of the heated matter where the two gases meet. In the case of a burning candle (Fig. 129), one of the bodies appears to be a solid, but a closer scrutiny of the phenomenon shows that the solid does not burn directly. A combustible gas is manufactured continuously by the heat of the

combustion and rises from the wick. The introduction of a narrow tube into the interior of the flame enables us to draw off a stream of this gas and to ignite it at a remote point. Thus, a flame is a phenomenon produced at the surface where two gases meet and undergo combination with the evolution of heat and more or less light.

In the chemical point of view, it is a matter of indifference whether the gas outside the flame contains oxygen, and the gas inside consists of substances ordinarily known as combustibles, or whether this order is reversed. In an atmosphere of ordinary illuminating-gas, the flame must be fed with air. This condition is easily realized (Fig. 130). The lamp-chimney is closed at the top until it has become filled with illuminating-gas. After the lapse of a few minutes this can be ignited as it issues from the bottom of the wide, straight tube which projects from the interior. When the hole in the cover of the lamp-chimney is then opened, the upward draft causes the flame of the burning gas to recede up the tube, and there results a flame fed by air and burning in coal-gas. In an atmosphere of this kind, materials playing the part of a candle burning in air would have to be substances which, under the influence of the heat of combustion, give off oxygen. Strongly heated potassium chlorate, for example, appears to burn continuously in such an atmosphere when lowered into it in a deflagrating spoon.

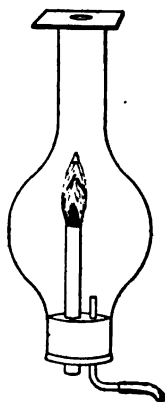


Fig. 130.

**Luminous Flames: Lampblack.**— The flame of hydrogen, under ordinary circumstances, is almost invisible, nearly all the energy of the combustion being devoted to the production of heat. A part of this, however, may be transformed into light by the suspension of a suitable solid body, such as a platinum wire, in the flame. The holding of a piece of quicklime in an oxyhydrogen flame (*cf.* p. 126) is a practical illustration of this method of securing luminosity. In general, luminosity may be produced by the presence of some solid which is heated to incandescence.

In the Welsbach lamp the flame itself is non-luminous and, but for the mantle, would be identical with the ordinary Bunsen flame. The mantle which hangs in the flame, however, by its incandescence, furnishes the light. This mantle is composed of a mixture of 99 per cent thorium dioxide  $\text{ThO}_2$  and one per cent cerium dioxide  $\text{CeO}_2$ . While many oxides would give out a white light, and could be obtained much more cheaply than these, they have not sufficient coherence to make their use practicable. These oxides act as a contact agent, hastening the combustion and liberation of heat close to their surface, and so acquire a temperature higher than the average for the rest of the flame. The Welsbach lamp gives four times as much light as does the same gas, issuing at the same rate, from an ordinary burner. It is worth noting that any appreciable variation from the above proportions, by the introduction of either more or less cerium oxide, produces a marked diminution in the intensity and whiteness of the light (see Thorium).

In cases of brilliant combustion, as of magnesium ribbon or phosphorus, a solid body is formed whose incandescence accounts for the light. The flame of ordinary illuminating-gas does not at first sight appear to give evidence of the presence of any solid body. But if a cold evaporating dish is held in the flame for a moment, a thick deposit of finely divided carbon (soot) is formed, and we at once realize that the light is due to the glow of these particles in a mass of intensely hot gas. Carbon is, indeed, an extremely combustible substance, and is eventually entirely consumed. But a fresh supply is continually being generated in the interior of the flame, while the oxygen with which it is to unite is outside the flame altogether. Thus the carbon particles persist until, drifting with the spreading gas, they reach the periphery of the flame.

On a large scale, oil residues are burned so that the flame strikes a revolving, iron vessel cooled with water. The soot or **lampblack** is continuously scraped off as the vessel turns.

Lampblack is used in making printer's ink, India ink, and black varnish.

It cannot be said that no flames are luminous unless a solid body is contained in them. When compressed hydrogen is burned in an atmosphere of oxygen under pressure, the light given out by the flame is much greater, and, in general, illuminating power seems to be heightened by increase in the concentration of the gas. In special cases, also, such as the explosion of a mixture of nitric oxide with carbon bisulphide vapor [Lect. exp.], a flame which has intense illuminating power is produced, although the density of the gases is low and solids are lacking.

**The Bunsen Flame: The Blast Lamp.**—In the burner devised by Robert Bunsen, a jet of ordinary illuminating-gas is projected from a narrow opening into a wider tube (Fig. 131). In this tube it becomes mixed with air, forced by atmospheric pressure through openings whose dimensions can be altered by means of a perforated ring. When the supply of air is sufficient, the flame becomes non-luminous. With a somewhat different construction, and the use of a bellows to force a larger proportion of air into the gas, a still hotter flame can be produced. The instrument in this case is known as a **blast-lamp**.

The high temperature of the **blast-lamp flame** presents an interesting problem. The same amounts of gas and air burn to give the same amounts of the same products, whether the air blast is on or off. The same amount of heat is produced, and the same quantities of the same substances are heated. The average temperature throughout the flame should therefore be the same. In point of fact, it is the same, but the stream of hot gas is *moving more rapidly* when the blast is going. The temperature of a body immersed in the flame depends, on the one hand upon the rate at which heat reaches it, and upon the other on the rate at which it loses heat by radiation. The heat is partly carried by the moving, heated gases (convection), and partly transmitted by conduction through the *stationary layer* (p. 503) on the surface of the body. Now, the latter is the slower process. Hence a rapid stream of gas, which leaves a thinner stationary layer, will diminish the distance the heat has to travel by con-

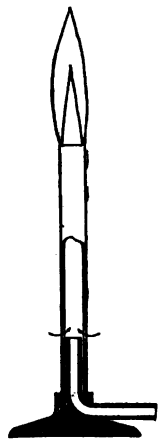


FIG. 131.

duction and so convey heat to the body faster than could a slow stream of the same temperature. Thus, with a blast flame, the loss by radiation is the same at the same temperature, but heat reaches the body faster and so the temperature of the body more nearly approaches that of the flame itself.

The Bunsen flame is hotter than an ordinary flame, because in it, also, the gases move faster. It is instructive to note the effect of forcing in larger and larger proportions of air into the Bunsen flame. The flame at the top of the tube continually diminishes in size, even after it has become non-luminous. Finally, a point is reached at which the flame is so unstable that the smallest further increase in the supply of air causes it to descend into the tube. The mixture of illuminating-gas and air in the tube of a Bunsen burner is an explosive one, and the explosion-flame will proceed through it with greater rapidity, the more nearly the quantity of air approaches that required for complete combustion. When the speed with which the

explosion-flame would move, equals that with which the stream of the mixed gases is coming upward through the tube, the flame reaches the unstable condition just mentioned. Any increase in the proportion of air raises the speed with which the explosion can travel, and the flame is thus able to proceed down the tube against the stream of gas. This phenomenon is frequently noticed in the Bunsen burner, when the holes admitting the air are too large, or a draft momentarily causes an increase in the supply of air. The flame **strikes back**, and thereafter continues to burn at the bottom of the tube.



FIG. 132.

**Structure of the Bunsen Flame.** — When an exceedingly small luminous flame is examined, the various parts of which it consists may easily be made out. In the interior there is a dark cone which is composed of illuminating-gas and air, and in it no combustion is taking place. A match-head may be held here for some time without being set on fire. This is therefore not properly a part of the flame. Outside this is a vivid blue layer (C, Fig. 132) which is best seen in the lower part of the flame, but extends beneath the luminous sheath, and covers the dark inner cone completely. Outside the blue flame, and covering the greater part of it, is the cone-shaped luminous portion (B). Over all is an invisible mantle of non-luminous flame (A), which becomes visible when the

light from the luminous part is purposely obstructed. In the luminous gas-flame, therefore, there are four regions, if we count the inner cone of gas. The difference between this and the non-luminous Bunsen flame is that in the latter the luminous region is omitted, and the inner, dark cone, the blue sheath, and the outer mantle, are the only parts which can be distinguished. We shall see that in these different regions the chemical changes taking place are different.

*The Causes of Luminosity and Non-Luminosity.* — The study of the chemical changes taking place in the Bunsen flame, particularly with the object of explaining (1) the luminosity of the flame of the pure gas, and (2) the non-luminosity of that produced by the same gas when it is mixed with air, has been the subject of many elaborate investigations. The questions are: (1) Why is carbon liberated in the former case, and (2) why is it not liberated in the latter? Let us consider these questions in order.

1. The investigations of Lewes (1892) and others show conclusively that the free carbon in the luminous zone of the ordinary flame is accompanied by free hydrogen, and that both are formed by dissociation of the ethylene in the inner blue cone. This substance, when heated, gives acetylene, and the latter then dissociates into carbon and hydrogen (p. 591):



The carbon glows, until, as it drifts outwards, it encounters the oxygen of the air and is burned. The first oxygen encountered combines more readily with the hydrogen, since it is a gas, than with the carbon, which is now in *solid* particles and therefore burns less readily. That carbon glows when heated in the absence of oxygen, without being consumed, is a fact familiar in the behavior of the incandescent electric lamp, the filaments of which were all formerly made of carbon.

The conception that when hydrocarbons burn, they first undergo dissociation, and then union with oxygen, is in harmony with what we have observed also in the case of the combustion of hydrogen sulphide, where the presence of free sulphur and free hydrogen in the interior of the flame was demonstrated (p. 416). That acetylene is actually formed as an intermediate substance is easily shown. It is found that when the Bunsen flame "strikes back," and the combustion of the gases is rendered incomplete by the contact of the

flame with the cold tube, a large amount of acetylene is formed. Again, when the gases surrounding the flame of air burning in illuminating-gas (p. 595) are withdrawn by means of a pump and caused to pass through an ammoniacal solution of cuprous chloride (Fig. 133), large quantities of copper-acetylide are precipitated.

2. The influence of the air admitted to the Bunsen burner, in interfering with this dissociation in such a way as to destroy all

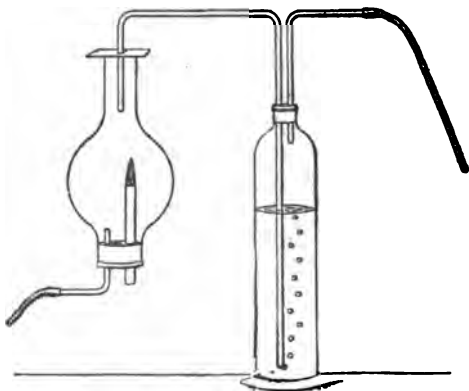


FIG. 133.

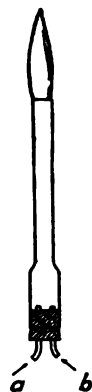


FIG. 134.

luminosity, is the most difficult point to explain. The effect is frequently attributed to the oxygen which the air contains. This view, however, is seriously weakened by a consideration of the undoubted fact that oxygen is not required. Carbon dioxide or steam is equally efficient when introduced instead of air (Fig. 134, gas enters at *a* and  $\text{CO}_2$  at *b*). Even nitrogen, which cannot possibly be suspected of furnishing any oxygen, likewise destroys the luminosity. Lewes has shown that 0.5 volumes of oxygen in 1 volume of coal gas destroy the luminosity. But 2.30 volumes of nitrogen or 2.27 volumes of air accomplish the same result. Thus the efficiency of air is not much greater than that of nitrogen, in spite of the fact that one-fifth of the former is oxygen.

It is evident that the effect is due, in part at least, to the *dilution* with a *cold* gas. This is confirmed by the observation that a cold platinum dish held in a small luminous flame is similarly destructive of the luminosity. If the tube of the Bunsen burner is *heated*, so that the mixed gases are considerably raised in temperature before reaching the non-luminous flame, the latter becomes lumi-

nous. It is probable, therefore, that the cold gas lowers the temperature of the inner flame, and at the same time the dilution diminishes the speed with which the free carbon is formed (Lewes). Even if the temperature is not reduced below that at which dissociation of the ethylene can occur, yet the dilution and cooling, together, prevent that sharp dissociation at this particular point which is necessary for the production of the great excess of free carbon needed to furnish light.

Before these investigations were made, a different answer was given to the question why the flame of pure illuminating gas contains free carbon and is luminous. It was said that hydrogen was more easily burned than carbon, and therefore the latter was left free, to be burned later. It is true that gaseous hydrogen burns more easily than *solid* carbon *e.g.*, charcoal. But in ethylene, *both* elements are equally gaseous and the explanation is faulty. Smithells (1892) demonstrated the falsity of this explanation by devising a *cone-separator* (Fig. 135). The air and ethylene or other gas are admitted in proportions which can be varied, and the mixture burns at the top of the wider tube. As the quantity of air is increased, however, the speed with which an explosion-flame would pass through it becomes greater, and finally the inner cone passes down and rests upon the mouth of the narrow tube through which the mixture of gases is issuing more rapidly. A preliminary combustion takes place in the blue cone, while the final conversion of the whole material into carbon dioxide and water is completed in the outer mantle. This remains at the top of the wider tube, where alone the necessary air can be obtained. By means of a side tube (not shown) he withdrew the inter-conal gas and found that, while all of the carbon was burned by the inner cone as far as carbon monoxide  $\text{CO}$ , most of the hydrogen was still entirely uncombined. This was the case, not only with illuminating-gas, which initially contains much free hydrogen, but also when the flame was fed with *pure methane*. The change in the inner cone of the Bunsen flame consists, therefore, mainly in the burning of all the hydrocarbons to carbon monoxide, with liberation of the hydrogen. In the outer cone, it is practically a burning of water gas that is taking place.

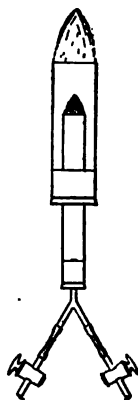


FIG. 135.



**Exercises.** — 1. Write a graphic formula for hexane.

2. Write an equation for the formation of aluminium carbide (p. 589).

3. Make a section showing the shape of the flame produced by burning hydrogen gas when the latter issues from a circular opening.

4. Name the radicals  $C_6H_{11}$ ,  $C_6H_{10}$ ,  $C_6H_9$ ,  $C_{16}H_{31}$ , and the substances  $C_6H_{11}Cl$ ,  $C_6H_{11}HSO_4$ .

## CHAPTER XXX

### THE CARBOHYDRATES, ORGANIC ACIDS, ALCOHOLS, SOAP, COLLOIDS, FOODS

A PLANT takes carbon dioxide from the air and water from the ground and, using the energy of sunlight, converts them into a growing framework of cellulose ( $C_6H_{10}O_5$ )<sub>n</sub> and, as we have seen (p. 580), into starch ( $C_6H_{10}O_5$ )<sub>n</sub>, which it stores in the cells. The cellulose of certain plants furnishes us with cotton, linen, jute, and paper. The starch of wheat, oats, maize (corn), and potatoes is one of the chief foodstuffs they contain. The plant, when dead and buried, changes into coal. The fresh wood, when distilled, supplies wood spirit (methyl alcohol) and other useful substances, and the residue is the valuable charcoal. Furthermore, from starch we can readily make sugar, alcohol, and other familiar materials. Cellulose, starch, and the sugars (*e.g.*, cane-sugar  $C_{12}H_{22}O_{11}$ ) contain oxygen and hydrogen in the same proportions in which they are present in water, 2H : 1O. They might be considered hydrates of carbon, and so they are called the carbohydrates. The foregoing brief summary shows that the **carbohydrates** introduce us to a much greater variety of interesting organic compounds than does petroleum.

#### THE CARBOHYDRATES

**Cellulose ( $C_6H_{10}O_5$ )<sub>n</sub> and Paper.** — The wall of each cell, and therefore the whole framework of a plant, is made of cellulose. Linen and cotton are pure cellulose. The walls of the cells are usually more or less thickened by a substance called **lignin**, which has much the same composition, but different chemical behavior. The best paper is made of cotton or linen (rag-paper). Cheaper kinds are prepared by cutting wood, such as spruce or pine, into chips and treating ("cooking") them with a solution of calcium bisulphite  $Ca(HSO_3)_2$ . This process decomposes the lignin, and converts it into soluble materials. The sulphite liquor is then run off, and the pulpy material is washed, beaten with water to reduce it to minute shreds, and bleached with very dilute chlorine-water. The pure cellulose, now **paper-pulp**, is suspended in

water, spread on screens, pressed, and dried. During the process, other substances are added. Thus, size (gelatine or rosin and alum, see Sizing) prevents the ink from running; pulverized calcium sulphate (gypsum), clay, and other white solids ("loading") give body to the paper and permit the production of a smooth surface by rolling ("calendering"). Dyestuffs can be added to give special tints. Filter paper is pure cellulose.

The sulphite lyes, after neutralization of the acids, and other treatment, can be fermented with yeast to give alcohol (see p. 607). Pure cellulose gives no sugar, so that the alcohol comes from decomposition products of the lignin.

**Starch** ( $C_6H_{10}O_5$ )<sub>n</sub>. — Starch consists of little colorless granules of various rounded shapes (Fig. 136), which are easily seen under the microscope. These granules are massed in large quantities in the ears of wheat and oats, in the tubers of potatoes, in the grains of maize (corn), and in peas and beans. Even in the leaves they can be seen. Starch is recognized by the iodine test (p. 276), turning deep blue with a trace of free iodine.



FIG. 136.

The treatment of wheat flour, which is three-fourths starch, by washing out the starch through porous cloth with water, has already been described (p. 5). Starch is made from maize in America and from potatoes in Europe, by washing the flour on sieves.

Starch is *not* soluble in water. If boiled with water, however, the granules swell and break and the starch is diffused through the water, giving a clear liquid. If too much water is not used, the liquid when cold sets as a jelly. While the liquid is hot, much of the starch will pass through a filter along with the water. Such a liquid is called a **colloidal suspension**. Suspensions like this are constantly met with in using complex organic compounds like jellies, glues, soaps, and dyes. Even insoluble inorganic materials, like gold, give such suspensions (see p. 621).

The colloidal suspension of starch turns blue when a solution containing free iodine is added to it. It is **used** in the laundry for stiffening white goods. Glucose is manufactured from it.

**Glucose**  $C_6H_{12}O_6$ , a Sugar, from Starch. — When starch is boiled with water, to which a few drops of an acid (contact agent),

such as hydrochloric acid, have been added, the liquid, after neutralization of the acid, is found to be sweet. One of the sugars, glucose  $C_6H_{12}O_6$ , can be obtained in crystals after evaporation. The crystals form "brewers' glucose" and the syrup produced by concentration is **corn syrup** (if maize is the source of the starch). The latter, although less sweet than ordinary sugar, is much less expensive and is used in making preserves and cheap candy.

The molecular weight of starch is unknown, but undoubtedly large. The formula  $(C_6H_{10}O_5)_x$  shows the composition. The water, in presence of a little acid, decomposes the molecules and combines with the material. First, dextrin (used as paste or mucilage) is formed and this breaks up into glucose. The action is an hydrolysis:



Glucose is known also as **dextrose** and as **grape sugar**. The crystalline granules in raisins (dried grapes) are composed mainly of it. When pure, it is almost colorless. It reduces cupric hydroxide, in Fehling's solution (*q.v.*), to cuprous oxide.

Corn syrup contains 30–40 per cent of unchanged dextrin, 40–50 per cent of glucose, and the rest water.

**The Sugars.** — The common sugars may be divided into the **monosaccharides**, usually with the formula  $C_6H_{12}O_6$ , and the **disaccharides**, usually  $C_{12}H_{22}O_{11}$ . Of these, the following will be referred to in what follows:

<b>Monosaccharides:</b>	<b>Glucose</b>	(grape sugar or dextrose) $C_6H_{12}O_6$ ,
	<b>Fructose</b>	(fruit sugar or levulose) $C_6H_{12}O_6$ .
<b>Disaccharides:</b>	<b>Sucrose</b>	(cane sugar, beet sugar) $C_{12}H_{22}O_{11}$ .
	<b>Maltose</b>	(action of malt on starch) $C_{12}H_{22}O_{11}$ .
	<b>Lactose</b>	(milk sugar, in animals only) $C_{12}H_{22}O_{11}$ .

**Sucrose, or Cane Sugar  $C_{12}H_{22}O_{11}$ .** — Plants, such as the sugar-cane and beet, besides forming cellulose and starch, produce exceptional amounts of **sucrose**, or table sugar. The sap of the sugar maple contains much of it.

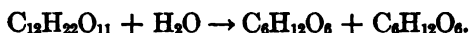
Cane sugar is extracted by crushing the stalks between rollers, and evaporating the expressed liquid (18 per cent sugar) in closed pans. A partial vacuum is maintained so that the solution may boil at a low temperature (65° to begin with) and none of the sugar be decomposed. When the syrup cools, the sucrose appears in

brown-colored crystals. The mother-liquor is called molasses. In the refinery, the sugar is redissolved, the solution is poured through a column of charcoal, which takes out the coloring matter, and the liquid is once more allowed to deposit crystals. Pure cane-sugar has a faint yellow tint, and a small amount of ultramarine (*q.v.*) is added to give that whiteness which is popularly connected with purity in sugar.

Sugar beets (16 per cent or more sugar) are sliced and steeped in water. The extract contains a gummy material in colloidal suspension. This is coagulated and precipitated by adding slaked lime (calcium hydroxide)  $\text{Ca}(\text{OH})_2$  suspended in water, and boiling. After separation of the clear liquid, carbon dioxide is passed through it to precipitate the excess of lime as carbonate  $\text{CaCO}_3$ . The solution is then decolorized with charcoal and evaporated to crystallization.

As regards properties, sucrose crystallizes in four-sided prisms (rock-candy, Fig. 73, p. 173) and melts at  $160^\circ$ . When heated to  $200\text{--}210^\circ$  it partially decomposes, leaving a soluble, brown, mixed material, **caramel**, used in coloring whisky and soups. Sucrose does *not* reduce Fehling's solution.

When boiled with water containing a trace of acid (contact agent), sucrose is hydrolyzed, giving a mixture of the two monosaccharides, glucose and fructose:



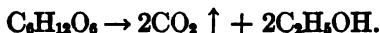
The process is called **inversion**, and the mixture **invert-sugar**. It is found in many sweet fruits and in honey. Each sugar interferes with the crystallization of the other, by lowering the freezing-point (p. 335), and so invert-sugar is added in making fondant candy and candy that is to be pulled, both of which must remain soft for some time. Icing for cakes has to some extent this property, and is made by adding acid substances to sugar, such as vinegar, lemon juice, or cream of tartar.

The action of the acid in inversion is catalytic, and the rate of this more or less leisurely chemical change depends upon the concentration of the hydrogen ions. It therefore furnishes one means of comparing acids as regards their chemical activity, and has the special advantage that the acid is not consumed during the process (*cf.* p. 295), but remains of constant concentration throughout the whole time.

**Enzymes.** — These are active organic compounds contained in certain vegetable organisms. The organisms may be divided into three classes, each secreting different enzymes, which confine themselves for the most part to special kinds of chemical change. (1) The **molds**, when grown in sugar solution or beef extract, or other nutritive solutions, produce decompositions known collectively as putrefaction. (2) **Certain bacteria** promote the oxidation of alcohol to acetic acid (see p. 609). Some also decompose sugar, furnishing butyric or lactic acid as one of the products. (3) The **yeasts** (*saccharomycetes*), decompose sugars into alcohol and carbon dioxide. They consist of microscopic cells, which, while multiplying, secrete within each cell two very active, soluble substances. These are **zymase** and **sucrase** (invertase), which belong to a class of organic substances called **enzymes**. Sucrase means an enzyme that splits sugar. Enzymes produce remarkable chemical changes by their mere presence (contact actions).

Enzymes which produce still other kinds of chemical change are found in the body, such as pepsin which hydrolyzes proteins in the stomach.

**Alcoholic Fermentation.** — When some yeast (*S. cerevisiae*), which is a mass of the living plants, is added to a solution of glucose at about 30°, the small amount of zymase gradually decomposes the sugar. Bubbles of carbon dioxide soon begin to rise, and may be tested (p. 501) with limewater (Fig. 137). At the same time, alcohol (ethyl alcohol  $C_2H_5OH$ ) accumulates in the liquid:



Yeast will ferment fructose  $C_6H_{12}O_6$  with the same result, but more slowly, so that, when placed in invert-sugar, it decomposes the glucose first and the fructose afterwards.

Zymase does not act upon sucrose (table sugar), but sucrase hydrolyzes the sucrose in the same way as does a dilute acid, giving invert-sugar. The latter is then decomposed by the zymase, and so cane-sugar in solution is fermented by yeast into alcohol and carbon dioxide, just as is glucose, only more slowly.

In making **wine**, the glucose contained in the grape juice is fermented by a species of yeast found on the skins of the grapes (*S. ellipsoideus*). The wine is allowed to stand, after fermentation, un-

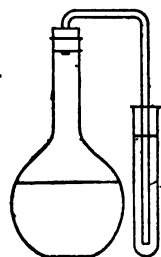


FIG. 137.

til it has deposited a considerable crust of material known as argol, which consists mainly of potassium-hydrogen tartrate  $\text{KHC}_4\text{H}_4\text{O}_6$ , cream of tartar. The concentration of the sugar in the grape-juice being small, the quantity of alcohol contained in the product is not very great. By distillation of wine, **brandy**, containing a much larger proportion of alcohol, is made. The special flavors of wines and brandies depend upon materials, other than sugar, originally contained in the fermented liquid, upon by-products of the fermentation, and upon materials which arise by slow chemical changes while the liquor is stored.

**Commercial alcohol** is not made from sugar, but from the starch of potatoes or maize. When barley is allowed to sprout, an enzyme, **amylase** (meaning starch-splitting enzyme) or diastase, is formed in the ears. The whole material is dried, and is then called **malt**. When this is mixed with starch and water, the amylase hydrolyzes the starch to maltose  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  (p. 605). The latter is then further hydrolyzed by yeast to form glucose  $\text{C}_6\text{H}_{12}\text{O}_6$ , and this is decomposed by the zymase into alcohol and carbon dioxide.

**Whisky** (about 50 per cent alcohol) is made by treating the starch of rye, maize, or barley in the same way, with subsequent distillation (see below) to separate the alcohol (whisky). **Beer** is made similarly from various kinds of grain, especially barley, but the fermented liquor is not distilled. Aside from the alcohol and carbon dioxide, considerable quantities of other substances extracted from the grain remain in the solution and form the so-called "extract," which varies in kind and quantity in different varieties of beer.

When used in bread-making, the yeast acts upon a trace of sugar in the flour, and the carbon dioxide gas evolved raises the bread.

**Ethyl Alcohol  $\text{C}_2\text{H}_5\text{OH}$ .**—Common alcohol is related to ethane  $\text{C}_2\text{H}_6$ , having an hydroxyl group in place of one unit of hydrogen. Hence its name.

Ethyl alcohol boils at  $78.3^\circ$  and so, when the fermented liquor is distilled (rectified) it is almost pure alcohol that comes off. Commercial alcohol contains 95 per cent by volume (in Great Britain, 90 per cent). **Absolute alcohol** cannot be made by distillation alone (see below). It is prepared by adding quicklime, which combines with the water, and redistilling the liquid.

Alcohol mixes with water in all proportions. In dilute, aqueous solution it is not ionized, and does not interact with acids, bases,

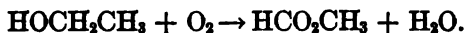
or salts. It is, however, easily oxidized to acetic acid. When water is absent, it interacts with acids slowly (see p. 617).

Alcohol is **used** as a solvent for the resins employed in making varnishes for wood and lacquers for metal.

On account of the high duty on 95 per cent alcohol (\$2.11 per gallon in the U. S. and 24/6 in Gt. Britain), **denatured alcohol** (methylated spirit), which is free of duty, is employed for industrial purposes. The alcohol (cost about 22 cents per gal. in the U. S. and 1/6 in Britain) is mixed with offensive or poisonous materials, which prevent its consumption as a beverage, without interfering with other uses. Wood spirit and gasoline are often employed.

**Distillation of Ethyl Alcohol.**—Mixtures of two liquids, when distilled, behave in one of three ways. Two of these have been described already (p. 212), and alcohol (b.-p. 78.30°) and water (b.-p. 100°) illustrate the third. In this case the vapor tension of a certain mixture is *higher* than that of any other mixture and higher than that of either component separately. This special mixture has, therefore, a *lower* boiling-point than any other. In the present instance this mixture contains 95.57 per cent of alcohol and 4.43 per cent of water and boils at 78.15°. When the fermented liquid, with its large percentage of water, is distilled, the alcohol all tends to pass off first, in association with that part of the water required to constitute the mixture of minimum boiling-point. Repeated distillation simply eliminates more completely the excess of water beyond this amount (viz., 4.43 per cent), by leaving it in the residues.

**Acetic Acid  $\text{HCO}_2\text{CH}_3$ .**—This is the sour substance in vinegar, and has many industrial applications. Vinegar is made by oxidizing alcohol with atmospheric oxygen, using an enzyme secreted by *bacterium aceti* (mother of vinegar) as contact agent. Oxygen alone does not affect alcohol in the cold. Dilute alcohol from any source, such as fermented apple juice (hard cider), is allowed to trickle over shavings in a barrel. Holes admit air, and the shavings are inoculated in advance by wetting with vinegar:



The issuing liquid contains 5–15 per cent of acetic acid, which can be purified by fractional distillation to separate the water. It boils at 118° and freezes at 16.7°. Although four atoms of hydro-



gen are contained in its molecule, but one of these is replaceable by metals. This fact is recognized in the reaction formula of the acid,  $\text{HC}_2\text{H}_3\text{O}_2$ , or  $\text{HCO}_2\text{CH}_3$ . It is a weak, monobasic acid:  $\text{HCO}_2\text{CH}_3 \rightleftharpoons \text{H}^+ + \text{CO}_2\text{CH}_3^-$ .

### WOOD, CHARCOAL, COAL, COKE

**Destructive Distillation of Wood. Charcoal.** — Dry wood is distilled in iron retorts, and the vapors coming off are led through a condenser to separate the liquids from the gases. The cellulose, lignin, moisture, and resinous material are decomposed or volatilized, and only charcoal remains. The gases, consisting mainly of hydrogen, methane  $\text{CH}_4$ , ethane  $\text{C}_2\text{H}_6$ , ethylene  $\text{C}_2\text{H}_4$ , and carbon monoxide  $\text{CO}$ , are employed, on account of their combustibility, as fuel in the distillation itself. The fluids form a complex mixture containing large quantities of water, methyl alcohol  $\text{CH}_3\text{OH}$  (wood spirit), acetic acid,\* acetone  $(\text{CH}_3)_2\text{CO}$ , and tar. The liquids can be separated. The methyl alcohol (wood spirit) is used in varnish making. The acetone has several uses (e.g., p. 593).

Wood charcoal exhibits the cellular structure of the material from which it was made, and is therefore highly porous and has an enormous internal surface. When the charcoal is burned, the mineral constituents of the wood appear in the ash. This is composed of the carbonates of the metallic elements present. For certain purposes, charcoals, made in the same fashion as the above from bones and from blood, find wide application. The former, called **bone black**, contains much calcium phosphate (p. 548). In the old method of making charcoal, which is still practiced, the wood was piled up, covered with turf, and set on fire. All the valuable volatile products were lost, as well as part of the charcoal itself.

In the laboratory, **pure carbon** is made by dissolving sugar in little water and adding concentrated sulphuric acid as a dehydrating agent:  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \rightarrow 12\text{C} + 11\text{H}_2\text{O}$ . The black mass is washed with water until free from the acid. The sugar is purified from mineral matter, before use, by crystallization from water.

**Properties of Charcoal.** — Charcoal is amorphous carbon (density variable, up to 1.8). It exhibits certain properties which are

\* The dry distillation of bones (see below), on the other hand, and of animal matter (p. 520) in general, gives alkaline liquids, because of the ammonia that is formed.

not shared by other forms of carbon. For example, it can take up large quantities of many gases. Boxwood charcoal will in this way absorb ninety times its own volume of ammonia, fifty-five volumes of hydrogen sulphide or nine volumes of oxygen. Freshly made dogwood charcoal (used in making the best gunpowder), when pulverized immediately after its preparation, often catches fire spontaneously on account of the heat liberated by the condensation of oxygen. It is therefore set aside for two weeks, to permit the slow absorption of moisture and air. The absorbed gases may be removed unchanged by heating the charcoal in a vacuum. The phenomenon, described as **adsorption**, is caused by the *adhesion* of the gases to the very extensive surface (due to porosity) which the charcoal possesses. Glass and all other solids show the same property, though in a smaller degree (p. 147). Solid and liquid bodies are also in many cases taken up by charcoal in a similar fashion. Thus, organic dyes, such as indigo, litmus, and cochineal, and natural coloring matters (see sugar refining, p. 606), which are all more or less colloidal in nature, are removed when the liquid is shaken with, or poured through pulverized charcoal. The organic materials dissolved in the drinking water also undergo adsorption in charcoal, but the charcoal soon becomes inactive. Charcoal is likewise used in reducing ores, and as a smokeless fuel.

**Coal.** — When vegetable matter decomposes, *without heating*, and while covered with sand or clay so that *air is excluded*, water and hydrocarbons are liberated, and the products are peat, or bituminous coal, or anthracite.

We are concerned mainly with the products obtained by distilling coal, to get coal gas and coke, and with its use as fuel. To determine its suitability for various purposes, the coal is analyzed, and its heating power is measured.

In **coal analysis**, the air-dried material is used. The *water* is determined by heating 1 g. at 105° for 1 hour. Much water lowers the fuel value, because heat is wasted in vaporizing it, and in decomposing it (*cf.* p. 577). After reweighing the sample, the coal is heated with the Bunsen flame in a covered crucible to drive off the *volatile matter*. After weighing again, air is admitted, and strong heat is applied to burn up the *fixed carbon* (coke). The residue is the *ash*. In the following table the proportions are compared with seasoned wood on the one hand, and with charcoal and coke on the other.

The **calorific power** of a coal determines largely its value for heating. A sample (about 1 g.) is burned in a bomb calorimeter (p. 98). The rise in temperature of a known weight of surrounding water gives the number of calories. The coal is set on fire by a wire heated electrically. Engineers use the number of British Thermal Units (1 B.T.U. = heat required to raise 1 lb. of water 1° F.) developed by 1 pound of coal. The number of B.T.U. =  $1.8 \times$  number of calories per gram of coal.

Bituminous coals give much, and widely varying amounts of volatile matter, while anthracite gives very little. The ash is the mineral matter of the original plants, with rock material in many specimens. For coal gas, and even for coke, a coal high in volatile matter is chosen. For water gas (p. 577) anthracite or coke is employed.

	Water.	Volatile matter.	Fixed carbon.	Ash.	Sulphur.	Cal. per 1 g.
Wood . . . . .	20.0	49.0	30.0	1.0	....	3,100
Peat . . . . .	20.0	51.6	25.0	3.2	0.2	4,270
Bituminous . . . . .	1.3	36.7	53.5	8.5	1.7	7,800
Semi-bituminous . . . . .	4.0	16.0	68.5	11	0.5	7,510
Anthracite . . . . .	3.0	5.6	80.5	10.9	0.8	8,000
Charcoal . . . . .	3.2	4.2	90.7	1.7	....	7,580
Coke . . . . .	2.5	1.3	86.3	12.4	1.3	7,770
Petroleum . . . . .	....	....	....	....	....	11,000

If the heat of combustion of a coal is known, the amount of steam it should furnish can be calculated. It takes 100 cal. to raise 1 g. of water from 0° C. to 100° C. and 540 cal. more to convert it into steam. If the quantity of steam is too small, the furnace, draft, or firing is defective. Too much draft, for example, merely adds additional, useless air to be heated. If the flue gas, when analyzed, contains only 3 per cent of carbon dioxide, instead of the normal 12 per cent, then for every ton of coal burned, 52 tons of unnecessary air were raised to the temperature of the furnace. Tests of this kind can control the efficiency of every device in a modern factory, and they ought to be in universal use.

**Coal Gas.**—The gas plant (Fig. 138) includes: (1) The fire-brick retorts in which the coal is heated to 1300°, (2) the hydraulic main, a wide iron pipe above them in which the tar collects, (3) the condenser and wash box for cooling and condensing oils, (4)

the scrubbers where the ammonia is taken out by water, (5) the purifier where hydrogen sulphide is absorbed by hydrated ferric oxide and (6) the holder where the gas collects.

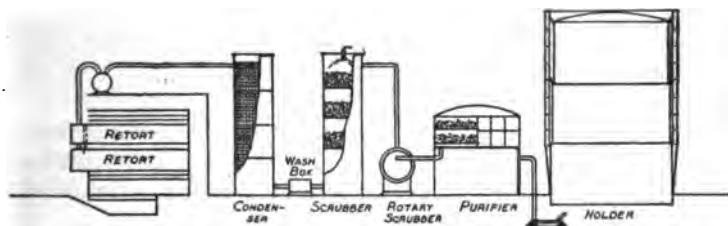


FIG. 138.

One short ton (2000 lbs.) of the bituminous coal in the above table gave: Gas 10,500 cu. ft. with 13 candle power, coke 1325 lbs., ammonia 5 lbs. (= 20 lbs.  $(\text{NH}_4)_2\text{SO}_4$  worth \$60 per ton), and tar 12 gallons. The components of the gas were: Illuminants 3.8, heating gases 90.2, impurities 6.0. Calorific power of gas 610 B.T.U. per cu. ft.; sp. gr. (air = 1) 0.43.

The tar is frequently distilled fractionally and yields: Benzene  $\text{C}_6\text{H}_6$ , from which aniline and many dyes and drugs are prepared; naphthalene  $\text{C}_{10}\text{H}_8$ , sold as moth-balls, and the starting point for synthetic indigo; anthracene  $\text{C}_{14}\text{H}_{10}$ , from which valuable dyes such as alizarin and indanthrene are made; phenol or carbolic acid (p. 527), a disinfectant, and other useful substances. A rougher separation yields tar and pitch, for road-making, preserving timber, and waterproofing roofs.

**Coke.** — The **beehive** coke oven is a brick structure shaped like a beehive, with an additional opening at the top. The coal which fills it burns with a limited supply of air. All the vapors and gas burn at the upper opening, and the ammonia and tar and combustible gas are therefore wasted (*cf.* p. 516).

The **by-product coke oven** is a good deal like a gas plant. The chief difference is that the heating is arranged so as to decompose as much of the volatile matter as possible, and cause it to leave its carbon in the retort. The gas is therefore poor in illuminants, but excellent as fuel. The ammonia and tar are diminished in amount, but still valuable products. The yield of coke is about 73 per cent of the original coal, against 66 per cent from the beehive oven.

Burning coke gives a higher temperature than does coal, be-

cause no heat is used in vaporizing moisture and volatile matter. For the same reason, it burns without flame. Because of these and other properties, it is employed in immense quantities in reducing ores of iron in the blast furnace, as well as for many other purposes.

### ORGANIC ACIDS AND SALTS

Thus far, one acid, acetic acid, and two alcohols, methyl and ethyl alcohol, have been mentioned. But there are whole series of organic acids and alcohols, corresponding to the series of hydrocarbons.

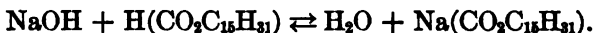
**Organic Acids and Their Salts.** — The general formula of the saturated series of **monobasic acids** is  $H(CO_2C_nH_{2n+1})$ . Thus:

Formic acid ( $n = 0$ ),  $H(CO_2H)$ . Palmitic acid ( $n = 15$ ),  $H(CO_2C_{15}H_{31})$ .  
 Acetic acid ( $n = 1$ ),  $H(CO_2CH_3)$ . Stearic acid ( $n = 17$ ),  $H(CO_2C_{17}H_{35})$ .  
 Butyric acid ( $n = 3$ ),  $H(CO_2C_4H_7)$ .

Formic (Lat. *formica*, an ant) acid is secreted by red ants. Formic (b.-p.  $100.1^\circ$ ), acetic, and butyric acids are liquids. Palmitic and stearic acids are solids, and are mixed with paraffin in making candles.

Acids containing less hydrogen are unsaturated. Thus, oleic acid ( $n = 17$ ) is  $H(CO_2C_{17}H_{33})$ .

The acids with large molecular weight are insoluble in water. All the acids, however, react with sodium hydroxide solution, giving soluble salts. Thus, palmitic acid gives sodium palmitate:



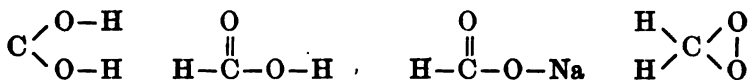
Other salts are sodium formate (p. 577)  $Na(CO_2H)$ , sodium acetate  $Na(CO_2CH_3)$ , sodium stearate  $Na(CO_2C_{17}H_{35})$ , sodium oleate  $Na(CO_2C_{17}H_{33})$ . Common soap is a mixture of the last two salts with sodium palmitate.

Later, in discussing fats and soap, it will be convenient to abbreviate the formulæ. A monobasic acid will be indicated by the formula  $HCO_2R$  and a salt by  $NaCO_2R$  or  $Ca(CO_2R)_2$ , where  $R$  stands for a hydrocarbon radical or group of atoms, such as  $C_nH_{2n+1}$ . In organic chemistry a radical is *not* always able to form an ion. Here the ion is  $CO_2R^-$ .

**Formic Acid  $HCO_2H$ .** — The removal of water from formic acid produces carbon monoxide (p. 577). Although we cannot

reverse the process and cause carbon monoxide to combine with water, yet by passing carbon monoxide over hot sodium hydroxide, we obtain sodium formate, from which formic acid may be liberated by double decomposition with another acid:  $\text{CO} + \text{NaOH} \rightarrow \text{NaCO}_2\text{H}$ .

This acid is secreted by red ants, and is found in stinging nettles. It is a liquid boiling at  $100.1^\circ$  and freezing at  $8.6^\circ$ . Although one of the weaker acids, it is much more active than acetic acid. The molecule contains two atoms of hydrogen, but the acid is, in fact, monobasic. The structural formula of the acid must take account of this fact. Three possibilities present themselves:



In the first and last the hydrogen units should behave alike. The second formula is the only one which expresses the replaceability of one unit and not of the other by a metal. Since the hydrogen in methane is not replaceable by metals (p. 588), we infer that the unit directly combined with carbon is the non-replaceable one. Sodium formate is therefore represented by the third formula.

**Acetic Acid  $\text{HCO}_2\text{CH}_3$ .**—This acid is produced in the dry distillation of wood (p. 610). Large quantities of it are manufactured from dilute alcohol (p. 609). The properties of acetic acid have already been described (p. 609).

Although four atoms of hydrogen are contained in its molecule, but one of these is replaceable by metals. This fact is recognized in the constitutional formula (p. 563) of the acid,  $\text{CH}_3\text{CO}(\text{OH})$ . In this acid a radical, methyl  $\text{CH}_3-$ , takes the place of H in formic acid.

Thus the group  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$ , called **carboxyl**, is contained in most carbon acids, and in each of them, as in formic acid, bears the replaceable hydrogen unit. The other three hydrogen units in acetic acid, however, are replaceable by chlorine, as is the case with the hydrogen units in hydrocarbons.

The above brief statements in regard to the mode of expressing the chemical properties of a substance by an elaborated formula bring out a tendency which prevails in the behavior of organic substances and is almost entirely lacking in inorganic chemistry. The units may be removed from the molecule of an organic substance one by one, and other units or groups may be substituted for them with-

out disturbing the rest of the molecule. The changes take place, not, as in the case of ionized substances, by the splitting of the molecule into two or more groups which act as wholes, but by the displacement of the units piecemeal and the introduction of new properties according to the nature of the groups introduced. Thus, if by any means we replace an atom of hydrogen by the carboxyl radical (see above), the product is an acid. If we replace it simply by the group OH the product is an alcohol. Each substitution may take place repeatedly in a given molecule, so that di-basic or tri-basic acids, di-hydric or tri-hydric alcohols (see Glycerine), or substances which contain both OH and  $\text{—COOH}$  in the same molecule (like lactic acid and tartaric acid), are formed. Other groups which may be introduced or removed are  $\text{—NH}_2$ ,  $\text{—NO}_2$ ,  $\text{—CN}$ , etc., each of which confers upon a substance the properties which go with the group, irrespective of the other features which the structure of the substance may already present.

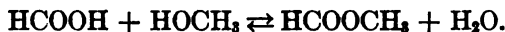
**Oxalic Acid  $\text{H}_2\text{C}_2\text{O}_4$ .** — This acid is dibasic, and consists of two carboxyl groups. Its calcium salt is the least soluble of the salts of calcium, and is found in many plants in the form of bundles of needle-shaped crystals. Potassium-hydrogen oxalate  $\text{KHC}_2\text{O}_4$  is found in the juices of various species of *oxalis*. The acid may be made by oxidation of sugar with nitric acid. The white crystals used in the laboratory are the hydrate  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . When heated carefully it sublimes unchanged. Stronger heating decomposes it into carbon dioxide and formic acid, and the latter breaks up, in part, into water and carbon monoxide. In the presence of dehydrating agents like sulphuric acid, water and the two oxides of carbon alone are formed (p. 577).

#### ALCOHOLS, ESTERS, FATS, SOAP, AND ETHERS

**Alcohols.** — We have already seen that when wood is distilled, **methyl alcohol** is found in the fluid product. When purified this is a colorless liquid boiling at  $66^\circ$ . Its solution in water shows no evidence of ionization. The formula  $(\text{CH}_3\text{OH})$  makes it impossible to represent the structure of the substance in more than one way. All alcohols contain the group  $\equiv \text{C} - \text{O} - \text{H}$  (cf. p. 616).

Common alcohol, **ethyl alcohol**  $\text{C}_2\text{H}_5\text{OH}$  (p. 607), is a member of the series  $\text{C}_n\text{H}_{2n+1}\text{OH}$ . There are also many alcohols with more than one OH group in each molecule. Of these, the one we shall presently encounter is **glycerine**  $\text{C}_3\text{H}_5(\text{OH})_3$ . The sugars and cellulose are alcohols with several hydroxyl radicals.

**Esters.**—When an organic acid and an alcohol are mixed, a very slow chemical action takes place, which, being reversible, in no case reaches completion. With the simplest members of these groups, formic acid and methyl alcohol, for example, the change is:



The product is known as **methyl formate**. This action has the appearance of a neutralization (p. 389), but is different in several ways. Alcohol is not a base, and in aqueous solution it does not conduct electricity. Then, true neutralization takes place instantly, while the foregoing action, and all like it, proceed very slowly. Thus, although acetic acid is a true acid, it is not *here* interacting with a base.

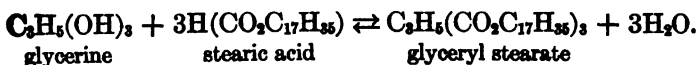
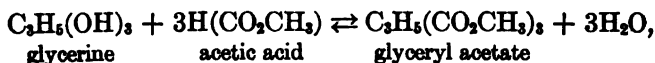
The corresponding action between acetic acid and ethyl alcohol:  $\text{CH}_3\text{COOH} + \text{HOC}_2\text{H}_5 \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$ , results in the formation of **ethyl acetate**. In this case, when equivalent quantities of the initial substances have been used without any solvent, and a condition of equilibrium has been reached, two-thirds of the material is found to have been transformed into ethyl acetate and water. If we start with the latter materials in pure form, the same equilibrium point is reached, and one-third of the material is converted into acetic acid and alcohol.

The products are *named* as if they were salts, and are sometimes called ethereal salts, because they result from the displacement of the hydrogen of an acid by a radical. This designation, however, is not very happy, since the products are not ionized and possess none of the properties of salts. The special name **esters**, therefore, has been given to them. The action is always extremely slow and never complete, but it may be hastened and carried to completion by the introduction of some substance capable of absorbing the water and so preventing the reversal. Concentrated sulphuric acid, for example, or anhydrous cupric sulphate, may be used.

**Inorganic acids** also interact with alcohols to give **esters**. Thus, **nitroglycerine** (p. 528) is an ester, and should be called glyceryl trinitrate. The use of sulphuric acid to assist in the removal of the water is illustrated in the preparation of this substance. **Guncotton** (p. 528) is an ester of nitric acid also, for cellulose is a complex alcohol. **Ethyl-hydrogen sulphate** (p. 591) is an ester of sulphuric acid. In this case the action may be made complete by using sulphuric acid containing an amount of sulphur trioxide sufficient to combine with the water to be produced.



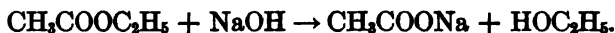
With the assistance of a dehydrating agent, similar actions take place between any alcohol and any acid (organic or inorganic). For example:



The glyceryl radical  $\text{C}_3\text{H}_5^{\text{III}}$  is trivalent, and takes the place of three atoms of hydrogen.

The above actions, in which an ester, like ethyl acetate, is formed, may be almost completely reversed if a sufficient amount of water is added (*cf.* p. 617). The hydrolysis of the ester is hastened by the presence of free acids in the water. This is owing to the catalytic action of the hydrogen ions, and the acceleration is proportional to the activity of the acid used. The acid, however, although it hastens the action, does not carry it beyond the condition of equilibrium which it would eventually have reached with the same amounts of the ester and of water alone.

When an ester is boiled with a strong base, such as sodium hydroxide solution, the salt of the acid and an alcohol are formed:



With more complex esters the sodium salts of the acids thus produced are known as **soaps**, and this general kind of action is called, therefore, **saponification** (Lat. *sapo*, soap). The speed with which it proceeds may be used as a means of measuring the activity of bases.

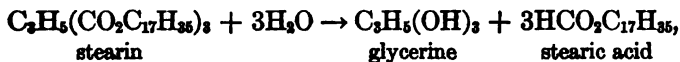
**Fats and Animal and Vegetable Oils.**—The fats and oils found in animal tissue, or pressed from seeds of plants, are composed mainly of esters. Beef **fat** is a mixture of about three-fourths glyceryl palmitate (palmitin)  $\text{C}_3\text{H}_5(\text{CO}_2\text{C}_{15}\text{H}_{31})_3$  and glyceryl stearate (stearin)  $\text{C}_3\text{H}_5(\text{CO}_2\text{C}_{17}\text{H}_{35})_3$ , along with one-fourth glyceryl oleate (olein)  $\text{C}_3\text{H}_5(\text{CO}_2\text{C}_{17}\text{H}_{33})_3$ . **Lard** (hog fat) contains a much larger proportion of the last (60 per cent) and is therefore softer. **Butter** contains the same esters, along with some water and some glyceryl butyrate (butyrin)  $\text{C}_3\text{H}_5(\text{CO}_2\text{C}_4\text{H}_7)_3$ . **Olive oil** contains much olein (75 per cent). **Cottonseed oil** is similar in composition, and is used as a substitute for olive oil, or for butter in cooking.

All these fats and oils contain certain proportions of the *free*

*organic acids* (see p. 625). These oils must not be confused with mineral oils, which are mixtures of hydrocarbons.

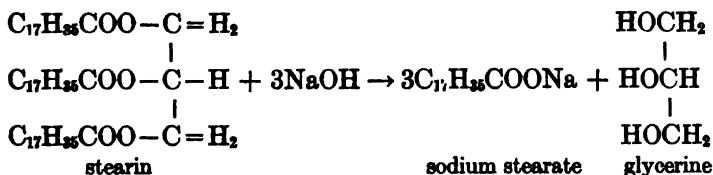
As regards **physical properties**, these oils are all insoluble in water, and the heavier ones also in cold alcohol. They dissolve readily, however, in ether, benzine, carbon disulphide, and carbon tetrachloride. Hence, benzine is used in dry-cleaning clothing made of silk or wool. The two last solvents are used in extracting vegetable oils.

**Chemical Properties of Fats and Oils.**—All fats and oils when boiled with water, and more rapidly when heated (200°) with water in a closed vessel, are decomposed. The ester is hydrolyzed, and the actions in the four equations last given (pp. 617, 618) are reversed. Thus, with stearin:



and when the mixture is cooled, the acid, being insoluble in water, forms a solid cake, while the glycerine is in solution in the water. If a mixture like beef fat is heated with water in this way, a mixture of palmitic, stearic, and oleic acids is obtained. The oleic acid (liquid) is pressed out, and the residue is mixed with paraffin to make candles. The glycerine is separated from the water and used in making nitroglycerine (glyceryl nitrate, an ester) and in medicine.

When fat is mixed with hot sodium hydroxide solution, it first forms an emulsion, in which the fat is disseminated in minute droplets through the liquid. This is a result of surface tension. When the emulsion is boiled, the fat is slowly decomposed into sodium palmitate, stearate, and oleate, and glycerine. The change is precisely similar in plan to the action on ethyl acetate (p. 618).

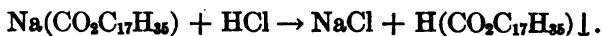


When common salt is added to the solution ("salting out"), the sodium salts of the three acids (the soap) are coagulated and separated as a floating layer, which solidifies when cold. The glycerine is contained in the salt solution.

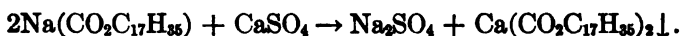
With potassium hydroxide, the potassium salts are obtained, and constitute **soft soap**.

The soaps are purified by redissolving in water and again salting out. Dyes and perfumes are often added. Floating varieties are made by beating the soap before it solidifies, and so introducing bubbles of air. Fine sand or pumice is added to make scouring soaps. Mixing with glycerine or sugar gives transparent soap.

**Chemical Properties of Soaps.** — Since the soaps are soluble salts of sodium, they are largely ionized in solution and interact with acids by double decomposition:

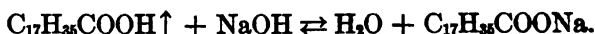


The acids are precipitated. They also enter into double decomposition with other salts. Thus, hard waters, containing compounds of calcium and magnesium in solution, give precipitates of the corresponding salts. For example:



Hence, with hard water, much soap is wasted in precipitating the "hardness."

These acids, not being soluble in water, have no effect upon litmus; but the fact that they are acids may be recognized when it is found that they are converted into soluble salts by soluble bases:

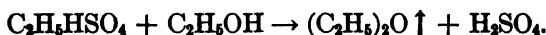


**Drying Oils.** — The oils, commonly used as "dryers" for mixing with varnish and paint and in making linoleum, such as linseed oil, hemp oil, poppy oil, and nut oil, contain esters of acids with unsaturated radicals. One of the constituents, for example, is the glyceryl ester of linoleic acid. The formula of this acid is  $\text{C}_{17}\text{H}_{31}\text{COOH}$ . It contains four hydrogen atoms less than the corresponding saturated acid (stearic acid). These oils, especially after having been recently heated, alone or with catalytic agents like lead oxide and manganese dioxide, absorb oxygen rapidly from the air, and become solid. They do not dry, in the ordinary sense, by evaporation.

**Ether.** — When two molecules of an alcohol lose one molecule of water, an ether is produced:



Thus, methyl alcohol gives **methyl ether**, and ethyl alcohol, **ethyl** or **common ether**. The action is most easily carried out by two steps. In making common ether, ethyl alcohol acts upon sulphuric acid, giving ethyl-hydrogen sulphate (p. 591); and the latter, when warmed gently with excess of alcohol, gives ethyl ether:



The ether ~~escapes~~ as vapor and is condensed.

Ethyl ether is a volatile liquid boiling at  $35.6^\circ$ . It is largely used as a solvent for iodine, fats, and other substances not readily soluble in water, and as an anæsthetic.

### COLLOIDAL SUSPENSION. CLEANSING POWER OF SOAP

**Colloidal Suspension.**—To explain the cleansing power of soap, it is necessary to learn more about colloids, for soap in solution is essentially colloidal.

The simplest colloidal suspensions are those of metals like gold and platinum. They can be made by forming an electric arc between the points of two wires, while the points are immersed in water. Liquids of various colors, depending on the degree of **dispersion** (fineness of the particles) of the metal, are thus formed. Such a liquid, (1) leaves no deposit on filter paper, (2) shows no elevation in the boiling-point of the solvent and, (3) no depression in the freezing-point. (4) The suspended body has little or no tendency to diffuse into a layer of the pure solvent. In consequence, if the colloidal solution is placed in a diffusion-shell, which is a test-tube shaped tube of filter-paper or parchment, immersed in water, none of the colloid escapes through the pores of the shell. Ordinary solutes escape more or less quickly, according to their molecular weight. Hence, a diffusion shell can be used to *separate* a mixture of colloidal and non-colloidal material. Thus, salt, if present with colloidal starch, or sugar if present with colloidal gold, can be removed by changing the water round the shell until no more salt (or sugar) is found to come out. This process is called **dialysis**, and was devised by Graham.

(5) The most striking property of colloids is shown by the **ultramicroscope**. In a perfectly darkened room, a converging beam of strong light is sent horizontally through the liquid (Fig. 139) and the place where the light is focussed is viewed from above, through a microscope. Under such circumstances, a true solution

remains perfectly dark, but a colloidal suspension shows minute points of light, first studied by Tyndall. Colloidal gold, solutions of soap, starch, gelatine, and dyes, and many other liquids exhibit the phenomenon. The points of light, due to particles which, although minute, contain many molecules, show also a trembling or vibrating movement, first noticed by a botanist Brown (1827) and called the **Brownian Movement**. The motion is due to collisions of the moving molecules of the solvent with the suspended particles of the colloid and, when the suspension is very fine (highly "disperse"), the particles shoot about rapidly.

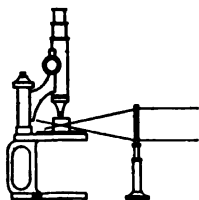


FIG. 139.

Other properties of colloidal suspensions are discussed below.

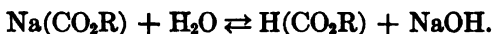
**Theory of Colloidal Suspension and Coagulation.** — When wires from a battery are immersed in the liquid, the particles of a colloid are found to move slowly either with or against the positive current. The phenomenon is called **electrophoresis**. Apparently, the colloidal particles are aggregates of molecules of an insoluble substance, collected round one or more ions. The particles, although relatively large, move almost as rapidly as in ionic migration (p. 345). This affords an explanation of the fact that the particles remain suspended, and do not settle. They are individually so small that they are kept in motion by collisions with the molecules of the solvent. If they could unite into large aggregates — like the particles of a precipitate — they would separate like any ordinary, insoluble substance. But, having like electrical charges, they *repel* one another, and so remain separate and in suspension.

Now those colloids which have distinct electrical charges can be **coagulated** or flocculated, and so precipitated in the liquid, by adding a solution of an ionized substance. Thus, colloidal gold and other metals are negative, and an equivalent amount of a positive ion, usually  $H^+$ , is present also. When a salt is added, the positive ion of the salt attaches itself to the negative colloidal metallic particles, neutral bodies result, coagulation can now occur, and precipitation follows. Bivalent ions are more effective than univalent ones (see Arsenic trisulphide). Conversely, a positive colloid, like ferric hydroxide, is coagulated by the negative ion of a salt, and more easily the higher the valence of the negative ion. Furthermore, one colloid will coagulate another of opposite charge. Thus, metaphosphoric acid is a negative colloid when in solution,

while ortho- and pyrophosphoric acid are not colloidal. Albumin is usually a positive colloid. Hence (p. 560), metaphosphoric acid and albumin coagulate and precipitate one another, while the other two acids have no action on albumin.

Starch and gelatine are neutral colloids, and are not easily coagulated.

**Soap Solution Colloidal: Salting Out.** — Soap solution, under the ultramicroscope, is seen to contain suspended particles. A test with litmus also shows that the soap is partly hydrolyzed:



Being a salt of a little ionized acid, the negative ion of the soap tends to combine with the  $\text{H}^+$  of the water:  $\text{H}^+ + (\text{CO}_2\text{R})^- \rightleftharpoons \text{H}(\text{CO}_2\text{R})$ , leaving the ions of sodium hydroxide. Now the acid thus set free combines with the undissociated molecules of the salt to form an acid salt  $\text{NaH}(\text{CO}_2\text{R})_2$ . This acid salt is insoluble, but remains in colloidal suspension as a negative colloid. When a strong solution of common salt (or even excess of sodium hydroxide) is added, the positive ion  $\text{Na}^+$  is adsorbed by the negative colloid (the acid salt) and the latter is coagulated. In coming out as a precipitate, it seems also to adsorb most of the sodium hydroxide, so that the precipitate has the composition of soap.

It should be noted that salt solution, or even sodium hydroxide solution, will coagulate (salt out) the soap from a 0.5 per cent solution, as well as from a 20 per cent or a stronger solution. This is, therefore, not a case of precipitation by adding excess of one ion, for that occurs only in saturated solutions (see Chap. XXXIV).

**The Cleansing Power of Soap. Emulsions.** — As a cleanser, soap solution — or suspension, as we should now call it — has two properties. It removes oil and grease (insoluble liquids) by forming an *emulsion* with them. It also removes minute solid particles of dirt, by taking the dirt into *suspension* (next section).

When an oil, such as kerosene, is violently shaken with water, both liquids are broken into minute droplets, and an opaque mixture results. The droplets of each liquid, however, quickly join together and soon the mass clears up and shows the two liquids in separate layers. If, however, a colloidal suspension is used, instead of pure water, the droplets unite much more slowly, if at all, and a more or less permanent, opaque, rather viscous mass results. Such

a mixture of two mutually insoluble liquids is called an **emulsion**. Thus, a few drops of soap solution will cause the kerosene and water to remain much longer in the condition of an emulsion. Similarly, vinegar and olive oil, when vigorously beaten (French dressing) separate rather quickly into two layers. But if the yolk of an egg (colloidal) is added to the vinegar, a stiff, almost solid mass can be made (Mayonnaise dressing), which will remain permanently emulsified. In removing grease, therefore, *rubbing* with soap solution turns the grease into suspended droplets (emulsifies it), and so the grease can be washed away.

This behavior of a colloid can be **explained**. When the kerosene and water are divided into droplets, with a great increase in the total surface, and in the surface energy of both, the surface tension of water, which is great, favors the reunion of the drops, with diminishing surface, and dissipation of the surface energy. Now, while *ordinary*, dilute solutions have a surface tension close to that of water, colloidal solutions (such as 0.5 per cent soap solution) have a very low surface tension. Hence, the tendency to diminish the surface of droplets of soap solution, by coalescence, is slight and ineffective. Furthermore, as predicted by Willard Gibbs of Yale University, and proved by experiment, a colloid has the peculiarity that it tends to reach a higher concentration in the surface layer than it has elsewhere in the liquid. When the colloid has adjusted itself to a state of *equilibrium*, in this regard, *it resists a decrease in the surface* (which would increase its concentration beyond the equilibrium value), just as much as it resists an increase, which would *diminish* its concentration. The emulsion of a colloidal suspension with an immiscible liquid is thus a stable condition.

Experiments confirming this view are easily made. If a solution of a dye like methyl violet (colloid) be shaken violently, and the froth (large surface in proportion to quantity of liquid) be separated, it is found that the liquid produced by the subsidence of the froth (an emulsion with *air* is not permanent), is darker in shade, and contains more dye, than an equal amount of the original liquid. Soap solution, after being shaken likewise, contains relatively more soap in the froth than in the liquid.

**Adsorption of Colloidal Matter.** — As we have seen (p. 611), when liquids containing colloidal substances, such as dyes and natural organic coloring matters, are shaken with pulverized charcoal, the colloid is **adsorbed** by the charcoal — that is, it adheres to the

surface of the particles of the charcoal. This principle is used in decolorizing sugar (p. 606) and in "bleaching" oils. Now, soap is also removed from solution (suspension) by shaking with charcoal or with infusorial earth, in the same fashion.

Pulverized charcoal is, relatively, a coarse powder. If soot, which is very finely divided carbon, be freed from oil or grease by washing with ether, it gives a loose, non-caking powder. If this powder be shaken with water, it settles. If it be shaken with dilute soap solution, it remains in suspension, and the liquid resembles ink. The particles are so fine that, instead of carrying down the colloidal soap, and forming a precipitate, as charcoal does, they attach themselves to the colloidal soap, and remain suspended. This is therefore adsorption, with the difference from the ordinary phenomenon, that the colloid carries off the adsorbant, instead of the adsorbant carrying down the colloid. Now dirt is composed largely of soot, and equally fine particles of other substances. Hence, the soap first emulsifies the oil on the hands (or on soiled linen) and then adsorbs the particles of dirt which are thus set free.

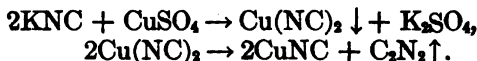
Formerly, soap solution was supposed to remove grease (and soot?) because of its slight alkaline reaction, due to hydrolysis. This explanation must be given up, because: (1) an alkali so dilute that it exists in equilibrium with the free fatty acid, can not possibly saponify the *ester* contained in a grease spot. (2) Pure alkali of the same concentration (or stronger) has no more emulsifying power than has water. Such an alkaline solution will indeed emulsify an animal or vegetable oil (cod-liver oil, cottonseed oil, castor oil), but it does so by interacting with the free fatty acid always present in such oil (p. 618) and *forming therefrom a soap*. Such an alkaline solution does *not* emulsify kerosene, and does not emulsify natural oils from which the free fatty acids have been removed with sodium hydroxide solution, although soap solution does. The emulsifying agency in this case is a soap. (3) Very dilute alkali has no more effect upon soot than has water, — but soap solution takes clean (greaseless) soot instantly into permanent suspension. (4) An aqueous solution of saponin  $C_{22}H_{44}O_{18}$ , obtainable from several plants, although it contains no alkali, lathers, emulsifies, and adsorbs dirt, just as does soap. It is a colloid.

#### CYANOGEN

**Cyanogen  $C_2N_2$ .** — This compound, being endothermal, is formed in small amount when a discharge of electricity takes place



between carbon poles in an atmosphere of nitrogen (*cf.* p. 592). Cyanogen, as an endothermal substance, is more easily made as one product in an action which as a whole is exothermal (p. 312). It is prepared by allowing a solution of cupric sulphate to trickle into a warm solution of potassium cyanide. The cupric cyanide, at first precipitated, quickly decomposes, giving cuprous cyanide and cyanogen:



Cyanogen is a very poisonous gas with a characteristic, faint odor.

**Hydrocyanic Acid HNC.** — This acid, called also **prussic acid**, has the formula  $\text{HN}=\text{C}$ , and is most easily made by the action of an acid upon a cyanide (see Potassium cyanide), followed by distillation. It is a colorless liquid boiling at  $26.5^\circ$ . It has an odor like that of bitter almonds, and is highly poisonous. In aqueous solution it is an extremely feeble acid, and is hardly ionized at all. In consequence of this, potassium cyanide is markedly hydrolyzed by water, and its aqueous solution is strongly alkaline. The behavior of hydrocyanic acid shows it to be an unsaturated body, a fact which is taken account of in the above formula, and illustrated in the two following paragraphs.

**Cyanates and Thiocyanates.** — When potassium cyanide is fused and stirred with an easily reducible oxide, like lead oxide  $\text{PbO}$ , the metal (for example, the lead) collects at the bottom of the iron crucible in molten form, and **potassium cyanate**  $\text{KNC O}$  is produced:



**Cyanic acid**  $\text{H}-\text{N}=\text{C}=\text{O}$  is very unstable. **Ammonium cyanate**  $\text{NH}_4\text{CNO}$  is chiefly remarkable for its transformation into urea (p. 583).

When potassium cyanide in aqueous solution is boiled with sulphur or with a polysulphide (p. 421), it is converted into **potassium thiocyanate**  $\text{KNCS}$ . This salt, or **ammonium thiocyanate**  $\text{NH}_4\text{NCS}$ , is used in testing for ferric-ion on account of the deep-red color of ferric thiocyanate (*cf.* p. 292). The ammonium salt undergoes at  $170^\circ$  a transformation parallel to that of ammonium cyanate (p. 583), thiocarbamide (sulpho-urea) being formed.

Fulminic acid  $\text{H}-\text{O}-\text{N}=\text{C}$  (p. 541) is an isomer of cyanic acid (see also Calcium cyanamide).

## FOODS

Plants and animals contain substances which are similar in composition; such as sucrose and lactose (p. 605), starch and glycogen ( $\text{C}_6\text{H}_{10}\text{O}_5$ ), animal fats and vegetable oils (both esters). Albumins and other proteins are found in both. They differ, however, markedly in the sources of these substances. The plant uses simple materials, like carbon dioxide, water, and potassium nitrate. The animal can make no use of these substances — it must be fed on complex compounds.

**Foods.** — Since the animal is continuously eliminating carbon dioxide, moisture, compounds of nitrogen, salts, and other substances, and is also giving off heat, these materials must be replaced, and fuel must be furnished. Like the plant, an animal can absorb only dissolved material. But it prepares its own solutions in a remarkable laboratory, the *digestive tract*. The production of suitable soluble substances is called *digestion*.

The following table shows the chief components of animal food, and the proportions in which they are present in the chief foods used by man:

	Water.	Protein.	Fat.	Carbo- hydrate.	Ash.
Beef (lean) . . . . .	73.8	22.1	2.9	.....	1.2
Cod . . . . .	82.6	15.8	0.4	.....	1.2
Eggs . . . . .	73.7	14.8	10.5	.....	1.0
Milk* . . . . .	87.0	3.3	4.0	5.0	0.7
Butter . . . . .	11.0	1.0	85.0	.....	3.0
Cheese (cheddar) . . . . .	27.4	27.7	36.8	4.1	4.0
Oatmeal . . . . .	7.3	16.1	7.2	67.5	1.9
Wheat flour . . . . .	11.9	13.3	1.5	72.7	0.6
Beans (dried) . . . . .	12.6	22.5	1.8	59.6	3.5
Almonds . . . . .	4.8	21.0	54.9	17.3	2.0
Maize (green corn) . . . . .	75.4	3.1	1.1	19.7	0.7
Potatoes . . . . .	78.3	2.2	0.1	18.4	1.0
Lettuce . . . . .	94.7	1.2	0.3	2.9	0.9

\* The emulsified fat separates slowly as the cream; the protein (casein, colloiddally suspended in the skim milk) is coagulated by rennet and constitutes cheese; the carbohydrate (lactose, a sugar) is then left in the water, along with inorganic salts.

We observe that the common animal foods, except milk, containing lactose (p. 605), carry no carbohydrates (the ox liver contains about 2 per cent of glycogen); that potatoes and corn, when dried, are nearly all starch; that lean meat, dry, is all protein; that some seeds (wheat and beans) contain little fat, some (oats) much more fat, and some (almonds and nuts) a large amount; and that lettuce is mainly water, with useful inorganic salts in solution, and cellulose.

The **proteins**, several of which have been mentioned (pp. 520, 528, 547) are white, amorphous substances containing, besides carbon, hydrogen, and oxygen, a large proportion of nitrogen (16 per cent), some sulphur (1 per cent) and frequently iron and phosphorus as well.

**Digestion.** — The process of rendering the constituents of food soluble is like fermentation (p. 607) — it is performed mainly by enzymes. Each class of components is handled by one or more enzymes. Thus, **starch** (in bread and potatoes) is partly digested during mastication by ptyalin (an amylase, p. 608) in the saliva, and partly by amylopsin in the small intestine. The resulting maltose is decomposed into glucose by another enzyme, and passes into the blood, where it is oxidized, furnishing heat. In diabetes, much of the glucose escapes oxidation, and is eliminated. Again, the **fats** are hydrolyzed into the acids and glycerine by lipases (fat-splitting enzymes) in the bile, and the acids go into solution (probably colloidal). The acids and glycerine recombine to form fats in the blood, and are either deposited in the tissues or oxidized. Finally, the **proteins** are changed in a similar way into peptones which are soluble in water, and in this form are able to pass through the wall of the intestine.

**Fuel Value of Food.** — Although food is required to replace waste, much of it is needed to furnish energy, by its oxidation, so that muscular movements may be maintained, and the temperature of the body kept up to its normal value (37° C.). Thus, the **fuel values** of foods are important. The average fuel values, expressed in *large calories* (1 Cal. = 1000 cal. as previously defined, p. 98), per gram, are:

Carbohydrates, 4 Cal.    Fats, 9 Cal.    Proteins, 4 Cal.

The fuel values *per pound* (453.6 g.) are 453.6 times greater.

Healthy life cannot be maintained on one kind of food—a

mixed diet is necessary. In general, it is held that 100 g. of proteins (giving 400 Cal.) per day, and a sufficient amount of other foods to give a total fuel value of 2200 Cal. is enough for a person doing no physical labor. When physical labor is involved, larger values, up to 3800 cal. per day, are necessary. The data in the table (p. 627) will enable one to calculate the fuel value of 100 g. (or of 1 lb.) of each kind of food.

**Exercises.** — 1. Make the graphic formulæ of methyl acetate (p. 615), ethyl formate, ethylene bromide (p. 591), oxalic acid (p. 616), ethyl ether (p. 621).

2. Make equations for the hydrolysis of starch to maltose (p. 608), the saponification of olein (p. 618).

3. Prepare a **summary** of the various statements that have been made in the text about **catalysis** (e.g., pp. 97, 128, 217, 222, 413, 433, 445, 516, 570, 606, 607, 618), and illustrate fully.

4. Calculate the fuel value of 1 lb. each of (a) oatmeal, (b) potatoes, (c) lettuce.

5. Calculate the weights, both in pounds and in grams, of 100 Cal. portions of, (a) eggs, (b) wheat flour, (c) almonds, (d) lettuce.

6. At current market prices, what would be the cost per 100 Cal. portion of beef, cod, butter, and wheat flour, respectively?

7. Why are there no colloidal suspensions of iron or zinc in water?

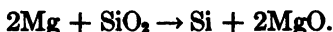
## CHAPTER XXXI

### SILICON AND BORON

IN respect to **chemical relations** there is a close resemblance between silicon and carbon. Silicon gives a monoxide, but is quadri-valent in all its other compounds. It is strictly a non-metallic element.

**Occurrence.** — Silicon, unlike carbon, is not found in the free condition. In combination it is the most plentiful element after oxygen, and constitutes more than one-quarter of the crust of the earth. The oxide is silica or sand  $\text{SiO}_2$ , and this oxide and its compounds are components of many rocks. In the inorganic world silicon is the characteristic element to almost as great an extent as is carbon in the organic realm.

**Preparation.** — When finely powdered magnesium and sand are mixed, and one part of the mass is heated, a violent action spreads rapidly through the whole:



At the same time, and especially if excess of the metal is used, some magnesium silicide  $\text{Mg}_2\text{Si}$  is formed also. The mixture is treated with a dilute acid which decomposes the magnesium oxide and the silicide, and leaves the **silicon** (**amorphous**) undissolved.

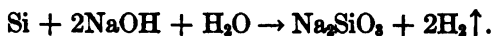
When amorphous silicon is dissolved in molten zinc, the mass, after solidification, is found to contain **crystalline silicon**. This form may be made in one operation, by heating three parts of potassium fluosilicate  $\text{K}_2\text{SiF}_6$  with one part of sodium and four parts of zinc in a closed crucible. The sodium displaces the silicon and combines with the fluorine, while the zinc acts as a solvent as before. The zinc is removed by the action of a dilute acid, the silicon remaining unaffected.

Silicon and **ferrosilicon** (an alloy of iron and silicon) are now made on a large scale, the former by heating sand and carbon, the latter by heating a mixture of ferric oxide and sand with carbon in the electric furnace (p. 569).

**Properties.** — **Amorphous silicon** is a brown powder. It unites with fluorine at the ordinary temperature, with chlorine at 430°, with bromine at 500°, with oxygen at 400°, with sulphur at 600°, with nitrogen at about 1000°, and with carbon and boron at temperatures attainable only in the electric furnace. It is slowly oxidized by *aqua regia* to silicic acid, and is dissolved by a mixture of hydrofluoric acid and nitric acid, giving silicon tetrafluoride.

**Crystallized silicon** consists of black needles belonging to the regular system, and is less active than the other variety. It oxidizes superficially at 400°, and the dioxide formed on the surface hinders further action. With chlorine and fluorine it unites easily when heated. Gaseous hydrogen fluoride interacts violently with it at a high temperature, heat and light are given out, and silicon tetrafluoride and hydrogen are formed. It is slowly attacked by hydrofluoric acid mixed with nitric acid, but not by any others of the oxygen acids.

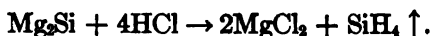
Silicon and ferrosilicon act readily upon a cold solution of sodium hydroxide (*cf.* p. 122), the metasilicate being formed:



This is one of the sources of hydrogen for filling balloons and airships. A layer of petroleum on the surface prevents frothing. **Hydrogenite** is a mixture of ferrosilicon and dry sodium hydroxide, to which water is added drop by drop. Three kilograms give one cubic meter of hydrogen.

Silicon seems to be more active than carbon, for, when it is heated with fused potassium carbonate, potassium silicate is formed and carbon is liberated. Both kinds of silicon differ from carbon in being fusible at a very high temperature. The solidified product is crystallized silicon.

**Silicon Hydride  $\text{SiH}_4$ .** — Silicon differs from carbon in giving two well-defined compounds with hydrogen,  $\text{SiH}_4$  and  $\text{Si}_2\text{H}_6$ . The former is liberated as a gas by the action of hydrochloric acid upon magnesium silicide:



The action is similar to that by which hydrogen sulphide is made. Since the magnesium silicide always contains free magnesium, hydrogen is liberated at the same time. By leading the gases through a tube surrounded by liquid air, the silicon hydride is reduced to liquid

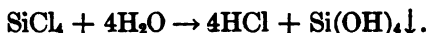
form, while the hydrogen passes on. The mixture with hydrogen is spontaneously inflammable. The pure gas becomes so only when its pressure is reduced (*cf.* p. 550). In the air, however, it is easily inflammable, by contact with a warm body. When heated, it decomposes into its constituents.

**Silicon Tetrachloride  $\text{SiCl}_4$ .**— This compound is made by direct union of the free elements. It is more conveniently prepared by passing chlorine over a strongly heated mixture of silicon dioxide and carbon. The gaseous products enter a condenser in which the tetrachloride assumes the liquid form:



Chlorine is unable to displace oxygen from combination with silicon, and has, therefore, when alone, no effect upon sand. In the above action, therefore, the carbon is used to secure the oxygen while the chlorine combines with the silicon. This kind of interaction is in some degree different from any which we have hitherto encountered. The principle underlying it was formerly used for making many chlorides (*e.g.*,  $\text{BCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{CrCl}_3$ ) from oxides, before simple ways of obtaining the elements in the free condition were known.

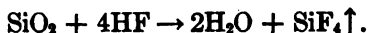
Silicon tetrachloride is a colorless liquid (b.-p.  $59^\circ$ ) which fumes strongly in moist air, giving silicic acid  $\text{Si}(\text{OH})_4$ . It acts violently upon cold water, and in this respect differs from carbon tetrachloride



The silicic acid (*q.v.*) soon appears as a gelatinous precipitate.

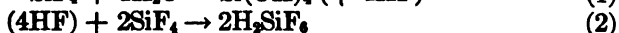
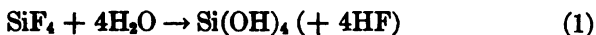
When silicon is heated in a stream of dry hydrogen chloride, a mixture of silicon tetrachloride and **silico-chloroform**  $\text{SiHCl}_3$  is produced. The latter is a volatile liquid boiling at  $34^\circ$ .

**Silicon Tetrafluoride  $\text{SiF}_4$ .**— When strong hydrofluoric acid acts upon sand, this gas is liberated:



Since the water interacts with the tetrafluoride (see below), the latter is usually made by the use of powdered calcium fluoride and excess of sulphuric acid. In this way the hydrogen fluoride is generated in contact with the sand, and at the same time the sulphuric acid takes possession of the water. Hydrofluoric acid acts in a corresponding way upon all silicates (*q.v.*), whether these are minerals or are artificial silicates like glass (*cf.* p. 283).

Silicon tetrafluoride is a gas which becomes solid, without liquefying (*cf.* p. 574), when cooled to  $-102^{\circ}$ . It fumes strongly in moist air, and acts vigorously upon water. This interaction is different from that of the tetrachloride, because the excess of the tetrafluoride forms a complex compound with the hydrofluoric acid:



The silicic acid is precipitated in the water, and may be separated by filtration, leaving a solution of **hydrofluosilicic acid**.

**Hydrofluosilicic Acid  $\text{H}_2\text{SiF}_6$ .**— This acid is stable only in solution. When the water is partly removed by evaporation, silicon tetrafluoride is given off, while most of the hydrogen fluoride remains to the last. Its salts are decomposed in a corresponding way when they are heated. This acid is used in analysis, chiefly because its potassium salt is one of the few salts of this metal which are relatively insoluble in water. The barium salt is also insoluble, but most of the salts of the heavy metals are soluble.

**Silicon Dioxide  $\text{SiO}_2$ .**— This substance may be made in the form of a white powder by heating precipitated silicic acid. It is found in many different forms in nature. In large, transparent, six-sided prisms, with pyramidal ends (Fig. 2), it is known as **quartz** or **rock crystal**. When colored by manganese and iron it is called **amethyst**, when by organic matter, **smoky quartz**. A special arrangement of the structure gives **cat's eye**. Amorphous forms of the same material, often colored brown or red with ferric oxide, are **agate**, **jasper**, and **onyx**, the last much used in making cameos. **Infusorial** or **diatomaceous earth (Tripoli powder)** is composed of the tests of minute organisms, and is used in scouring materials and for decolorizing oils. **Sponges** are also made of silica of organic origin. Slightly hydrated forms of silica are the **opal** and **flint**. A crystalline variety belonging to the hexagonal system, but showing entirely different crystalline forms, occurs occasionally in minute crystals, and is called **tridymite**.

Silica is found in the hard parts of straw, of some species of horsetail (*equisetum*), and of bamboo. In the form of whetstones it is used for grinding. The clear crystals are employed in making spectacles and optical instruments, and are more transparent to ultra-violet

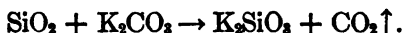


light than is glass. Pure sand is used in glass manufacture (*q.v.*). Infusorial earth, on account of the tubular form of many of the minute structures of which it is composed, can absorb three times its own weight of nitroglycerine, and is therefore employed in making dynamite. Recently, pieces of chemical apparatus have been manufactured by fusing quartz (m.-p. 1600°) in the oxy-hydrogen flame, or the electric furnace. The material does not crystallize on cooling, and is amorphous, like glass. Owing to the low coefficient of expansion of silica, the vessels can be heated to a red heat and chilled in cold water, without risk of fracture.

**Silicates. Water Glass.**—Silicon dioxide, although differing profoundly from carbon dioxide in its physical nature, nevertheless behaves like the latter chemically. Thus, when boiled with sodium hydroxide solution it forms sodium metasilicate  $\text{Na}_2\text{SiO}_3$  or orthosilicate  $\text{Na}_4\text{SiO}_4$ .

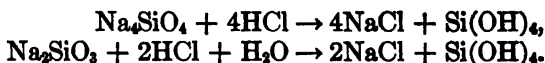


The salt is left as a gelatinous solid ("soluble glass") when the water is evaporated. The silicates of potassium and sodium may also be obtained by boiling sand with the carbonates of these metals, or, more rapidly, usually as metasilicates (see below), by *fusing* the mixture:



**Water glass** or soluble glass, being a salt of a feeble acid with an active base, gives an alkaline solution (pp. 399, 559). When manufactured for commercial use, it has the composition  $\text{Na}_2\text{Si}_2\text{O}_5$  ( $\text{Na}_2\text{SiO}_3, \text{SiO}_2$ ), which is less alkaline. It is used as a filler in cheap soaps, for fireproofing and waterproofing timber and textiles, and for preserving eggs.

**Silicic Acid  $\text{H}_4\text{SiO}_4$ .**—When acids are added to a solution of sodium silicate, silicic acid is set free. After a little delay it usually appears as a gelatinous precipitate. When, however, the silicate is poured into strong hydrochloric acid, no precipitation occurs. The silicic acid remains in **colloidal suspension**:



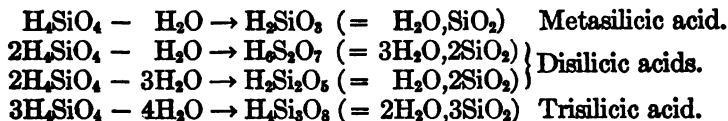
The gelatinous precipitate, when it has been dried, contains a smaller proportion of the elements of water. There seem to be no definite

stages, indicating the existence of various acids, such as we observe with phosphoric acid. We should expect the vapor tension of the water to decrease by steps, each of which should correspond to some acid of a particular degree of hydration (*cf.* p. 560), but, probably because it is amorphous while the phosphoric acids are crystalline, nothing of the sort is observed. The final product of drying is the dioxide.

Silicic acid is a very feeble acid. For this reason silicic acid can be completely displaced from its salts, even by so weak an acid as carbonic acid. Since the water in some geyser regions contains alkali silicates, the action of the carbon dioxide in the air causes deposition of silica round the places where the water issues from the ground. This form is known as *siliceous sinter*. Striking scenic effects, as in the white and pink terraces of New Zealand, are sometimes produced by this method of deposition.

The suspension of colloidal silicic acid can be freed from the acid and sodium chloride (see equation, above) by dialysis (p. 621). It is a positive or a negative colloid, according to the mode of preparation, and the two kinds are coagulated by addition of salts having bivalent negative and positive ions, respectively.

**Mineral Silicates.** — While, in the absence of definite knowledge, silicic acid is presumed to be the ortho-acid  $\text{Si}(\text{OH})_4$ , and no other silicic acids have been made, the salts are most easily classified by imagining them to be derived from various acids representing different degrees of hydration of the dioxide, or, to put it the other way, different degrees of dehydration of the ortho-acid. The following equations show the relation of the ortho-acid to some of the silicic acids whose salts are most commonly found amongst minerals:



Di- and trisilicates are those derived from acids containing two and three units of silicic anhydride, respectively, in the formula. The valences of the radicals of the acids are shown by the number of hydrogen units in the formulæ.

The composition of minerals is often exceedingly complex. This is due to the fact that amongst them mixed salts (p. 401) are very common, in which the hydrogen of the imaginary acid is displaced by

two or more metals in such a way that the total quantity of the metals is equivalent to the hydrogen. The following list presents in tabular form some **typical or common minerals**, arranged according to the above mentioned classification:

ORTHOSILICATES ( $H_4SiO_4$ )		METASILICATES ( $H_2SiO_3$ )	
Zircon,	$ZrSiO_4$	Wollastonite,	$CaSiO_3$
Garnet,	$Ca_3Al_2(SiO_4)_3$	Beryl,	$Gl_2Al_2(SiO_3)_6$
Mica,	$KH_2Al_3(SiO_4)_3$	Talc (soapstone),	$H_2Mg_3(SiO_3)_4$
Kaolin,	$H_2Al_2(SiO_4)_2 \cdot H_2O$	Asbestos,	$Mg_3Ca(SiO_3)_4$
DISILICATE ( $H_6Si_2O_7$ )		TRISILICATE ( $H_4Si_3O_9$ )	
Serpentine,	$Mg_3Si_2O_7 \cdot 2H_2O$	Orthoclase (felspar),	$KAlSi_3O_8$

It will be seen that the total valence of the metal units is equal to that of the acid radicals. Thus, in beryl there are six equivalents of glucinum (beryllium) and six of aluminium, taking the place of twelve units of hydrogen in  $(H_2SiO_3)_6$ .

**Garnets** are pulverized in manganese-steel crushers and used in making sandpaper. **Mica**, which is obtained in large sheets from Farther India, is used in making lamp-chimneys, for windows in stoves, and as an insulator in electrical apparatus. **Kaolin**, or **clay**, like mica, is an acid orthosilicate. It is formed in nature as the result of the action of water and carbonic acid upon minerals like felspar. In such cases, those elements which can form carbonates like potassium, magnesium, and calcium, are usually displaced from combination with the silicic acid. Aluminium, however, is too feeble a base to form a carbonate, and is thus left in combination as silicate. A clay containing lime is called a **marl**, and one containing sand, a **loam**.

Some of these minerals frequently occur mixed together as regular components of certain igneous rocks. Thus, **granite** (p. 4) is a more or less coarse mixture of quartz, mica, and felspar. Frequently the oblong, flesh-colored or white crystals of the last are large and very conspicuous both in granite and in **porphyry**. In **basalt** the components are usually less easily visible to the eye. **Lava** is the name for any rock recently ejected from a volcano. **Pumice-stone** is the name given to the parts of the lava which are porous, having acquired this texture from the expansion of bubbles of gas consequent upon release of pressure. **Sandstone** is composed of sand cemented together by clay or by calcium carbonate, and colored brown or yellow by ferric oxide.

The high melting-point of silica, compared with carbon dioxide, and the formation of these complex silicates, indicate that the oxide is highly associated  $(\text{SiO}_2)_x$ .

The hydrated silicates are decomposed by hydrochloric acid, but the others are not affected by acids, or are affected with extreme slowness. Hence special means have to be taken to get the constituents of such minerals into soluble form for the purpose of analysis. Two methods are in use. Sometimes the finely powdered mineral is heated in a platinum dish with hydrofluoric acid until all the silicon has passed off in the form of the tetrafluoride. Since the use of the fluorides would lead to difficulties in the course of the analysis, the resulting mixture of fluorides of the metals is next heated strongly with concentrated sulphuric acid, and the mixture of sulphates thus produced is treated according to the usual routine. In other cases the finely powdered mineral is fused at a bright red heat with a mixture of potassium and sodium carbonates. In this way carbonates of the metals are formed, along with potassium and sodium silicate. Treatment with water dissolves the latter, and leaves the carbonates to be handled in the usual way.

### BORON

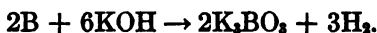
As regards **chemical relations**, boron, being a uniformly trivalent element, is a member of the aluminium family. Yet it is a pronounced non-metallic element, and its oxide and hydroxide are almost wholly acidic; aluminium is a metal, and with its oxide and hydroxide basic properties predominate. Boron and its compounds really resemble carbon and silicon and their compounds in all chemical properties, excepting that of valence.

**Occurrence.** — Like silicon, boron is found in oxygen compounds, namely, in boric acid (*q.v.*) and its salts. Of the latter, sodium tetraborate  $\text{Na}_2\text{B}_4\text{O}_7$ , or borax, came first from India under the name of **tincal**. It constitutes a large deposit in Borax Lake in California. Colemanite,  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ , from California, and other complex borates, furnish a large part of the commercial supply of compounds of boron.

**Preparation.** — When boric oxide is heated with powdered magnesium:  $\text{B}_2\text{O}_3 + 3\text{Mg} \rightarrow 3\text{MgO} + 2\text{B}$ , amorphous boron can be separated with some difficulty from the borides of magnesium in the resulting mixture. When excess of powdered aluminium is used, hard

crystals of boron, containing aluminium, are found in the solidified metal. They may be separated by interaction of the metal with dilute hydrochloric acid.

**Properties.** — Amorphous boron is a black powder. It unites with the same elements as does silicon (p. 631), but with somewhat greater activity. Like carbon (p. 425), it is also oxidized by hot, concentrated sulphuric or nitric acid, the product being boric acid. The crystalline variety is less rapidly attacked in each case. Both kinds interact with fused potassium hydroxide, giving a borate:



**Hydrides and Halides of Boron.** — When magnesium boride  $Mg_2B_3$  is treated with hydrochloric acid, a gas containing much hydrogen, and two hydrides of boron,  $B_4H_{10}$  and  $B_2H_6$ , is given off.

By combined action of carbon and chlorine on boric oxide, using the principle employed in preparing silicon tetrachloride (p. 632), the trichloride of boron  $BCl_3$  may be made. It is likewise formed by direct union of the free elements. It is also made easily by heating boric acid and phosphorus pentachloride, the action being an example of the behavior of the latter towards hydroxyl compounds (cf. p. 555):



The products are separated by fractional distillation. Boron trichloride is a liquid which boils at  $18^\circ$ , fumes strongly in moist air, and is completely hydrolyzed by water.

**Boron trifluoride**  $BF_3$  is made by the interaction of calcium fluoride and sulphuric acid with boron trioxide. The mode of preparation and the properties of the substance recall silicon tetrafluoride (p. 632). It interacts with water, like the latter, giving boric acid and hydrofluoboric acid  $HF_4$ :



The boric acid, not being very soluble, is precipitated. Hydrofluoboric acid is known only in solution, although many of its salts are stable.

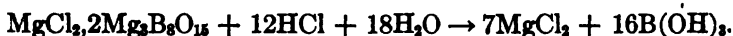
**Boric Acid**  $H_3BO_3$ . — Boric acid (boracic acid) is somewhat volatile with steam (cf. p. 563), and is found in Tuscany in jets of water vapor (*soffioni*) which issue from the ground. Water, retained

in small basins by brickwork, is placed over the openings, and from this water, after evaporation by the help of the steam of the soffioni themselves, boric acid is obtained in crystalline form. As boric acid is a very feeble acid, and withal little soluble, it may be made by mixing sulphuric acid and concentrated borax solution, and cooling:

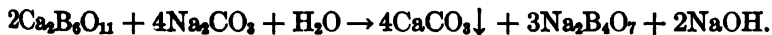


Boric acid crystallizes from water in thin white plates, which are soapy (like graphite and talc) to the touch. Its solubility in water is 4 parts in 100 at 19° and 34 in 100 at 100°. The solution scarcely affects litmus. The green tint it confers on the Bunsen flame is used as a test. At 100° the acid slowly loses water, leaving **metaboric acid**  $\text{HBO}_2$ , and at 140° **tetraboric acid** is formed:  $4\text{HBO}_2 - \text{H}_2\text{O} \rightarrow \text{H}_2\text{B}_4\text{O}_7$ . Strong heating gives the **trioxide**  $\text{B}_2\text{O}_3$ . When dissolved in water, these dehydrated compounds revert to boric acid. The solution of boric acid in water is used as an antiseptic in medicine (half-saturated, 2 per cent solution) and sometimes as a preservative for milk and other foods.

**Borates.** — Borates derived from orthoboric acid are practically unknown. The most familiar salt is **borax** or **sodium tetraborate**. The decahydrate  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , which crystallizes from water at 27° in large, transparent prisms, and the pentahydrate which crystallizes at 56°,\* are both marketed. They are made by crystallization of native borax. In Germany, borax is prepared from boracite, found at Stassfurt, by decomposing a solution of the mineral with hydrochloric acid:



The boric acid is redissolved in boiling water, and sodium carbonate is added:  $4\text{B}(\text{OH})_3 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{B}_4\text{O}_7 + 6\text{H}_2\text{O} + \text{CO}_2$ . In California it is made from colemanite by interaction with sodium carbonate:

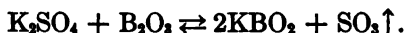


Since boric acid is a feeble acid, borax is hydrolyzed by water, and the solution has a marked alkaline reaction (*cf.* p. 399). In a 0.1*N* solution (25°), 0.5 per cent is hydrolyzed.

\* For explanation of the relation of temperature of crystallization to degree of hydration, see under Manganous sulphate.

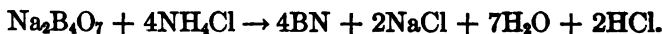
When heated with oxides of metals, sodium tetraborate behaves like sodium metaphosphate (*cf.* p. 560), and is used in the form of **beads** in analysis. If its formula be written  $2\text{NaBO}_2 \cdot \text{B}_2\text{O}_3$ , it will be seen that a considerable excess of the acid anhydride is contained in it, and that, therefore, a mixed metaborate may be formed by union with some basic oxide. Thus, with a trace of cupric oxide, the bead is tinged with green, from the presence of a compound like  $2\text{NaBO}_2 \cdot \text{Cu}(\text{BO}_2)_2$ . Cobalt compounds give a deep-blue color to the bead. For the same reason, borax is used in hard soldering. The hard solder (brass) is placed, with a little borax, upon the joint between the objects of copper or brass which are to be soldered. At the temperature produced by the blast-lamp the borax dissolves the superficial coating of oxides, and the molten solder is able to "wet" the clean surfaces. In welding iron, borax is scattered on the parts, and combines with the oxide to form a fusible mixed borate, which is forced out by the pressure. A substance used thus, to bring infusible bodies into a fusible form of combination, is called a **flux**. Borax is also mixed with glass in making enamels for cooking utensils.

**Boron Trioxide.** — The oxide, as made by heating boric acid, is a glassy white solid. It is obtained also by burning boron in oxygen. Being almost perfectly involatile, it is able, when heated with salts, to displace other acid anhydrides which can be vaporized:



It has a slight tendency to act as a basic oxide. With fuming sulphuric acid it gives a boryl pyrosulphate  $\text{BO} \cdot \text{HS}_2\text{O}_7$  which is decomposed by water, and with phosphoric acid a phosphate  $\text{BPO}_4$  which is stable.

**Nitride and Carbide.** — One of the difficulties in making free boron is due to its very great affinity for nitrogen, with which, when heated in the air, it unites to form a **nitride**  $\text{BN}$ . This compound is more easily made by heating borax with ammonium chloride:



The nitride is a white solid which is easily decomposed when heated in a current of steam (*cf.* p. 514):  $\text{BN} + 3\text{H}_2\text{O} \rightarrow \text{B}(\text{OH})_3 + \text{NH}_3$ .

A **carbide** of boron  $\text{B}_2\text{C}$  is made by heating the free substances in the electric furnace. It is harder than carborundum, and stands next to the diamond in respect to hardness.

**Exercises.** — 1. Why is the fact that carborundum  $\text{SiC}$  (p. 572) is not affected by water or acids worthy of mention?

2. Compare and contrast the elements carbon and silicon, and their corresponding compounds.

3. Formulate (p. 382) the interaction between aqueous solutions of an ammonium salt and of sodium orthosilicate.



## CHAPTER XXXII

### THE BASE-FORMING ELEMENTS

THERE are two ways in which the chemistry of a given set of elements may be described. We may take up the elements in succession, and discuss under each its physical and chemical properties, and the manufacture and behavior of a certain number of its compounds such as the oxide, hydroxide, nitrate, and sulphate. Or we may arrange our major classification according to the properties and the forms of combination, and detail the facts about the same set of elements under each. Both methods have such advantages that neither can be sacrificed entirely. We shall, therefore, adopt the former plan for our division into chapters, following the usage already employed for the non-metallic elements. In the present chapter a preliminary view of the chemistry of the metals will be given according to the second method.

*Physical Properties of the Metals.* — A knowledge of the physical properties of the metals is, to the chemist, of the greatest importance in connection with their manufacture and treatment. The following brief statement in regard to some of these properties is illustrative rather than exhaustive. It should be noticed that the properties of a metal vary according as the specimen has been prepared by rolling, casting, or some other process. Numerical values, therefore, when given, are only approximate.

Metals show what is commonly called a **metallic luster**, but, as a rule, they do so only when in compact form. Magnesium and aluminium exhibit it when powdered, but, in this condition most of the metals are black. In compact masses the metals are usually silvery white in color. Gold and copper, which are yellow and red respectively, are the conspicuous exceptions.

The metals can all be obtained in **crystallized form**, when a fused mass is allowed to cool slowly and the unsolidified portion is poured off. In almost all cases the crystals belong to the regular system. With the metals most nearly allied to the non-metals, however, they do not. Thus, the crystals of antimony and bismuth belong to the hexagonal system, and those of tin to the square prismatic.

The metals vary in **density** from lithium, which is little more than half as heavy as water (sp. gr. 0.53), to osmium, the density of which is 22.5. Those which have a density less than 5, namely, potassium, sodium, calcium, magnesium, aluminium, and barium, are called the light metals, and the others the heavy metals.

Most metals are **malleable**, and can be beaten into thin sheets without loss of continuity. Those which are allied to the non-metals, however, such as arsenic, antimony, and bismuth, are brittle, and can be reduced to powder in a mortar. Zinc becomes malleable only when heated to 150°. The order of the elements in respect to this property, beginning with the most malleable, is: Au, Ag, Cu, Sn, Pt, Pb, Zn, Fe, Ni.

The **tenacity** of the metals places them in a different order. It is measured by the number of kilograms which a piece of the metal 1 sq. mm. in section can sustain without breaking. The values are as follows: Fe 62, Cu 42, Pt 34, Ag 29, Au 27, Al 20, Zn 5, Pb 2.

The **hardness** (Appendix II) is measured by the ease with which the material may be disintegrated by a sharp, hard instrument. Potassium is as soft as wax, while chromium is hard enough to cut glass.

The **temperature** at which the metal **fuses** has an important bearing on its manufacture. Most of the following **melting-points** are only approximate:

Mercury . . . .	-39°	Zinc . . . . .	419°	Cast iron . . .	1150°
Potassium . . .	62°	Antimony . . .	630°	Manganese . . .	1260°
Sodium . . . .	97°	Magnesium . . .	651°	Nickel . . . . .	1452°
Tin . . . . .	232°	Aluminium . . .	659°	Chromium . . . .	1520°
Bismuth . . . .	271°	Silver . . . . .	960°	Iron (pure) . . .	1530°
Cadmium . . . .	321°	Gold . . . . .	1063°	Platinum . . . .	1755°
Lead . . . . .	327°	Copper . . . . .	1083°	Tungsten . . . .	3540°

It will be seen that mercury is a liquid, that potassium and sodium melt below the boiling-point of water, and that the metals down to the foot of the second column can be melted easily with the Bunsen flame. The metals osmium, molybdenum, uranium, iridium, and vanadium have melting-points above that of platinum. For iron, two different methods give 1510° and 1550°, respectively.

The methods of manufacture and the treatment of metals are much influenced also by their **volatility**. The following are easily distilled: Mercury, b.-p. 357°; potassium and sodium, b.-p. about 700°; cadmium, b.-p. 770°; zinc, b.-p. 920°. Even the most involatile metals can be converted into vapor in the electric arc.

In many cases molten metals dissolve in one another freely. The mixtures are called **alloys**, and in some cases are simply solid solutions. Sometimes, as in the case of lead and tin, mixtures can be formed in all proportions. On the other hand, the solubility may be limited, as in the case of zinc and lead, where only 1.6 parts of the former dissolve in 100 parts of the latter. Frequently chemical compounds are formed. The colors of alloys are not the average of those of the constituents. Thus, a mixture containing copper with 30 per cent of tin is perfectly white. A similar mixture with 30 per cent of zinc is pale yellow. The nickel alloy used in coining contains 75 per cent of copper and 25 per cent of nickel, yet it shows none of the color of the former. Thirty per cent of gold may be added to silver without conferring any yellow tint upon it.

Some of the properties of alloys are classifiable by the ordinary laws of solution. Thus, a foreign solute lowers the vapor tension of a solvent (p. 197), and so the presence of a foreign metal diminishes the ease with which particles can be torn from the surface by any means whatever. That is to say, it increases the hardness. A foreign metal also lowers the melting-point (p. 199, see solder). In many cases the metal becomes less active when alloyed. Thus, a mixture of gold and silver containing twenty-five per cent of the latter does not interact visibly with nitric acid. It is necessary to bring the amount of silver up to 75 per cent at least ("quartation") in order that the silver may be freely attacked by the warm acid. The gold remains in any case untouched. The malleability and the conductivity for heat and electricity are diminished by solution of a foreign metal. Copper, whose commercial applications depend largely on the first and third of these properties, is much affected in respect to them by the presence of even small traces of impurities.

Alloys in which mercury forms one of the components are known as **amalgams** (Gk. *μάλαγμα*, a soft mass), and are formed with especial ease by the lighter metals. Of the common metals, iron is the least miscible with mercury.

The good **conductivity** of metals for **electricity** distinguishes them with some degree of sharpness from the non-metals. They show considerable variation amongst themselves, silver conducting sixty times as well as mercury. The conductivity increases as the temperature is lowered, and this fact is taken advantage of in the measurement of the temperature of liquefied gases. The platinum resistance thermometer consists chiefly of a wire of platinum. The resistance of this metal diminishes so rapidly, with decreasing temperature, that

measurement of its resistance can be used for the accurate determination of the temperature. In the following table the conductivities of the metals are expressed in terms of the number of meters of wire 1 sq. mm. in section which, at 15°, offer a resistance of one ohm:

Silver, cast . . . . .	62.89	Nickel, cast . . . . .	7.59
Copper, commercial . . . .	57.40	Iron, drawn . . . . .	7.55
Gold, cast . . . . .	46.30	Platinum . . . . .	5.7-8.4
Aluminium, commercial . . .	31.52	Steel . . . . .	5.43
Zinc, rolled . . . . .	16.95	Lead . . . . .	4.56
Brass . . . . .	14.17	Mercury . . . . .	1.049

The resistance at 0° of a column of mercury 1 sq. mm. in section and 1.063 meters long is the unit of resistance, and is called one ohm. It is employed in expressing the conductivities of solutions (p. 362). To compare the above figures with those given for solutions, however, it must be recalled that, in the measurement of the conductivities of the latter, a column only 1 cm. in length and of 1 sq. cm. area was employed, so that the figures representing the conductivities of solutions are on a scale approximately ten thousand times as great as those presented in the above table. Thus, normal hydrochloric acid (p. 365) has a conductivity on the above scale of 0.0301, or less than a thirtieth of that of mercury.

The world's production (1913) of the metals in metric tons of 1000 kilos. is approximately as follows:

Copper	1,000,000	Chromium	50,000	Gold	680
Zinc	1,000,000	Nickel	32,000	Bismuth	500
Lead	1,000,000	Silver	7,800	Cadmium	50
Tin	120,000	Tungsten	4,800	Platinum	9
Aluminium	79,000	Mercury	3,000		

### **General Chemical Relations of the Metallic Elements.**—

Since most of the compounds of the metals are ionogens, their solutions, except when the metal is a part of a compound ion or of a complex ion (see below), all contain the metal in the ionic state, and the resulting substances, such as potassium-ion and cupric-ion, have constant properties, irrespective of the nature of the negative ion with which they may be mixed. The properties of the ions, simple and compound, are much used in making tests in analytical chemistry. On the other hand, the chemical properties of the oxides and of the salts in the *dry state* are of importance in connection with metallurgy.

There are **three chemical relations** which are characteristic of **all metallic elements**. These form the basis of the distinction between metallic and non-metallic elements. The first two of them have already been discussed somewhat fully.

1. The metals are able by themselves to form *positive radicals* of salts, and, therefore, to exist alone as positive ions (pp. 356, 375).

2. The oxides and hydroxides of the metal are basic (pp. 149, 374).

3. Each *typical* metal has at least one halogen compound which is little, if at all, hydrolyzed by water (p. 399 and next section). The same thing is true of nitrates and other salts involving active acids.

There are **three other chemical relations** which are shown by **many metallic elements**, but no one of them applies to all.

4. An oxide or hydroxide which is basic may also be acidic, as, for example, zinc hydroxide (p. 122). Even when this is not the case, some other oxide of the metal may be acidic exclusively, as is manganese heptoxide (p. 457). In consequence of either of these facts, a metal may form *part* of the negative radical of a simple salt, and therefore be found in a negative ion, as,  $\text{HZnO}_2^-$  or  $\text{MnO}_4^-$ .

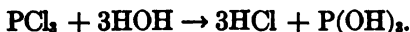
5. Some salts of certain metals combine with those of others to give complex salts (p. 405 and see p. 649). Of this sort are the complex cyanides, such as  $\text{K}.\text{Ag}(\text{CN})_2$  and  $\text{K}_4.\text{Fe}(\text{CN})_6$ . A metal thus forms part of the negative radical of a salt of a complex acid, and therefore is found in an *anion* like  $\text{Ag}(\text{CN})_2^-$  or  $\text{PtCl}_6^-$ .

6. Some metals also form parts of complex cations which are contained in solutions of molecular compounds (p. 530). Thus, when  $\text{AgCl} \cdot 3\text{NH}_3$  is dissolved in water, or when ammonium hydroxide is added to a solution of a salt of silver, the positive ion is found to be  $\text{Ag}(\text{NH}_3)_2^+$  (see under Copper). (For a detailed illustration of the application of these six criteria, see discussion of the chemical relations in the nitrogen family, Chap. XLI.)

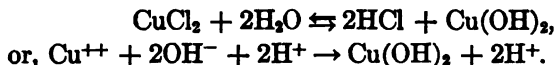
Aside from these points, many features in the behavior of metals and their compounds are summed up in the electromotive series (p. 404). The reader should re-read all the parts referred to above before proceeding farther. He should also re-examine the various kinds of chemical changes enumerated on p. 228 and particularly the varieties of ionic chemical change on p. 402.

***Hydrolysis of Halogen Compounds, Used to Distinguish Metallic Elements from Non-Metallic Elements.*** — We have seen that the halogen compounds of phosphorus (p. 555), of sulphur

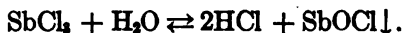
(p. 450), of silicon (p. 632), and of other non-metallic elements, are completely hydrolyzed by water, giving the hydrogen halide, and an acid which contains the hydroxyl of the water:



Now, those elements whose halogen compounds are *not* hydrolyzed by water, or, at all events, are only partly hydrolyzed, are the ones classed as metallic elements. Thus, sodium chloride is not decomposed appreciably by water, and cupric chloride, like cupric sulphate (p. 399), is but slightly hydrolyzed, and its solution has a faint acid reaction:



In a few cases, as with the chlorides of antimony (*q.v.*) and of bismuth (*q.v.*), a considerable proportion, but not all, of the halogen is removed from each molecule:



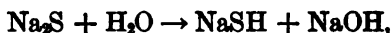
Here the water produces a slight hydrolysis, but the insolubility of one product weakens the reverse action and the equilibrium is displaced forwards chiefly because of the precipitation. The resulting mixture is strongly acid, and the product (antimony oxychloride) is a definite compound, of the nature of a mixed salt (p. 401), known as a basic salt. The difference is that, with the halides of the *metallic elements*, the action on water is notably *reversible*, and the reverse action, unless handicapped by precipitation of one factor, prevents much displacement of the equilibrium, while with halides of the *non-metallic elements*, the action is not reversible.

Hydrolysis of the halides of the metals is increased by rise in temperature and by dilution of the solution (addition of more water), and also gains headway when one of the products of hydrolysis is thrown down as a precipitate. The last two influences are the ones which normally permit any reversible action to approach completion (p. 301).

The halogen compounds are chosen as the basis of this criterion because the halogen acids are active and would reverse the hydrolysis completely, and leave no acid reaction, if the result depended upon them alone. It is the lack of activity in the base, and the tendency of its *molecules* to be formed from the metal ions of the salt and the  $\text{OH}^-$  of the water (p. 399), that determine the slight hydrolysis,

when it occurs. Thus, this criterion is simply another means of recognizing whether or not the hydroxide of the element is a strong (much ionized) base, and its application gives, therefore, the same result in each case as does the employment of the second of the chemical characteristics of the metallic elements (see above).

Other, non-halide salts of the metals, even of the most active, may be extensively hydrolyzed by water. Thus, sodium sulphide is decomposed by it (p. 418) to the extent of one-half. But here the solution is *alkaline* in reaction:



owing to the small ionization of the  $\text{SH}^-$  ion, and the result is due to the feebleness of the acid  $\text{H}_2\text{S}$ . Indeed, the great activity of the base is demonstrated by the final reaction of the solution, and the metallic nature of sodium is therefore not impugned by the existence of hydrolysis *per se* in such a salt as this, but is rather confirmed.

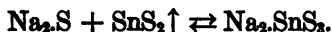
**To sum up:** An alkaline reaction shows that we have a solution of a salt of an active metal with a weak acid; an acid reaction that we have a salt of an inactive metal, which may even verge on the non-metallic, with an active acid. Salts of two active components give neutral solutions. Thus, as a particular case, the halogen compounds of the typical metals are not perceptibly hydrolyzed by water, and the hydrolysis of the halide of a less pronounced metal takes place with acid reaction, and is easily reversible by excess of either product. A salt of an acid and base both of which are weak is also hydrolyzed. If the resulting base or acid is insoluble, the hydrolysis may go nearly to completion. Aluminium carbonate and ammonium silicate are examples of salts which, for this reason, are completely hydrolyzed. From the former, aluminium hydroxide is precipitated, and from the latter silicic acid. When both base and acid are weak, but soluble, the resulting mixture may have an acid or a basic reaction, if the acid or the base is sufficiently active to affect an indicator. Thus, ammonium sulphide  $(\text{NH}_4)_2\text{S}$  solution is alkaline.

The rather exaggerated language commonly used by chemists in regard to hydrolysis must not be misinterpreted. When it is said that borax gives a strongly alkaline solution, and is "extensively" hydrolyzed, this only means that in a 0.1*N* solution 0.5 per cent of the salt is decomposed. Aluminium chloride gives a strongly acid solution, but even in a 0.001*N* solution the hydrolysis (25°) reaches only 4.5 per cent.

**Salts of Complex Acids.** — These salts are of many classes, and arise by direct union of two salts. Thus we have cyanides like potassium argenticyanide  $\text{K.Ag(CN)}_2$ , potassium cuprocyanide  $\text{K.Cu(CN)}_2$ , and potassium ferrocyanide  $\text{K}_4\text{Fe(CN)}_6$ :

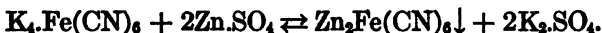


The complex sulphur compounds of arsenic, antimony, and tin (*q.v.*), such as sodium sulphostannate  $\text{Na}_2\text{.SnS}_3$ , are made in the same way:



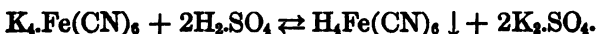
Many double halides are of a like nature, as potassium chloroplatinate  $\text{K}_2\text{.PtCl}_6$ , chloroplatinic acid  $\text{H}_2\text{.PtCl}_6$ , and sodium chloraurate  $\text{Na.AuCl}_4$ . In every case, the metal of one of the original salts is contained in the negative radical (the anion). Hydrofluosilicic acid (p. 633) is a compound analogous to those of the last group, excepting that  $\text{SiF}_4$ , from which it is formed, is not a salt, and silicon is not a metal.

The characteristic of these compounds is that, when they are ionized, the less positive metal is contained in a complex anion like  $\text{Ag(CN)}_2^-$ ,  $\text{SnS}_3^-$ ,  $\text{PtCl}_6^-$ . In fact, they behave, in most respects, like ordinary single salts. Thus, they undergo double decomposition in the normal manner, the complex ion acting as a whole. For example, a soluble ferrocyanide with a zinc salt gives zinc ferrocyanide:



This behavior distinguishes salts of complex acids from double salts (p. 402). In typical cases the latter resemble the former, indeed, only in their mode of preparation (by union of two simple salts), and in solution are resolved once more into the component salts and their separate ions. The distinction must be regarded, however, only as a means of rough classification for practical purposes. In reality, all complex ions give at least a trace of the simpler ions, and many are decomposed to a noticeable extent. At the other extreme, the double salts form complex ions in appreciable amounts in concentrated solutions.

In harmony with the above characteristic, salts of complex acids, like potassium ferrocyanide, when treated with acids, like sulphuric acid, undergo double decomposition, and give the free complex acid (here hydroferrocyanic acid):





But in many cases the acids are unstable, those of the cyanides, for example, giving up hydrocyanic acid and those of the complex sulphur compounds giving hydrogen sulphide:



The complex halogen acids, however, like  $\text{H}_2.\text{PtCl}_6$  and  $\text{H}.\text{AuCl}_4$ , are stable, and are fairly active as acids.

The similarity of these compounds to oxygen acids, and their salts, may be seen if we imagine them to be cases in which cyanogen, sulphur, chlorine, and other radicals have taken the place of oxygen in the anion. Thus,  $[(\text{CN})_2]^{II}$ ,  $[\text{Cl}_2]^{II}$ , and  $\text{S}^{II}$  are equivalent to  $\text{O}^{II}$ . Many of the corresponding oxygen compounds are actually known, as sodium stannate  $\text{Na}_2.\text{SnO}_3$  and sodium aurate  $\text{Na}.\text{AuO}_3$ , corresponding respectively to  $\text{Na}_2.\text{SnS}_2$  and  $\text{Na}.\text{AuCl}_4$ .

The behavior of complex ions is discussed further under Copper.

**Classification of the Metallic Elements by their Chemical Relations.** — In treating of the metallic elements and their compounds we shall use the groupings provided by the periodic system (p. 461). A division into eleven sets, which are described briefly and in general terms below, will be sufficient for the purpose of this book:

1. **Metals of the Alkalies.** — Lithium, sodium, potassium, rubidium, caesium, and the radical ammonium  $\text{NH}_4$ . These metals are univalent, and their oxides and hydroxides have strongly basic properties. Their salts with active acids are not hydrolyzed in solution.

2. **Metals of the Alkaline Earths.** — Calcium, strontium, barium, and radium. These metals are bivalent in all their compounds. Their oxides and hydroxides are strongly basic, but the latter are not so soluble in water as are the hydroxides of the former family. The salts with active acids are not hydrolyzed.

3. **Copper, Silver, and Gold.** — These metals occupy the right side of the second column of the table (opposite rear cover). Their alliance with the alkali metals, their neighbors, is remote. Each, however, gives compounds in which it is univalent, although, in their commoner compounds, copper and gold are bivalent and trivalent, respectively. The oxides and hydroxides of copper and gold have rather weak basic properties; those of silver are much more active.

4. **Beryllium, Magnesium, Zinc, Cadmium, and Mercury.** — These metals, occupying the right-hand side of the third column, are bivalent, although mercury forms a series of compounds in which it is

univalent as well. The oxides and hydroxides are feebly basic, those of magnesium being the most basic.

5. **Aluminium** and the other metals on both sides of the fourth column. — The metals of these groups are trivalent, and the oxides and hydroxides are feebly basic in character. The hydroxide of aluminium has also a feebly acidic tendency.

6. **Germanium, Tin, and Lead, and the Titanium Family.** — In accordance with their position in the periodic table these metals are all quadrivalent. At the same time they act also as bivalent elements, the compounds of this class in the case of lead being the more familiar. The oxides and hydroxides are feebly basic, and are able also to play the rôle of acidic oxides towards strong bases.

7. **Arsenic, Antimony, and Bismuth, and the metals of the Vanadium Group.** — These elements, like nitrogen and phosphorus, form two sets of compounds in which they are trivalent and quinquivalent, respectively. The acidic tendency of the oxides and hydroxides, which in the last column was noticeable, is here much more pronounced. Both oxides of arsenic are almost wholly acidic in behavior, and the pentoxides of the other elements are likewise acid anhydrides exclusively. The trioxides are basic in a feeble way, and their salts are much hydrolyzed by water.

8. **Chromium, Molybdenum, Tungsten, and Uranium.** — These elements, occupying the left-hand side of the seventh column, exhibit a considerable variety of valence. The maximum, however, is six in each case. The oxides of the form  $\text{CrO}$  and  $\text{Cr}_2\text{O}_3$ , in which the elements are bivalent and trivalent, are base-forming. Those of the form  $\text{CrO}_3$ , in which the elements are sexivalent, resemble sulphur trioxide and are acid anhydrides.

9. **Manganese.** — This element, the only one in the eighth column which has not yet been treated, gives several series of compounds in which its valance varies from 2 to 7. Compounds derived from the basic oxide  $\text{MnO}$  are the salts in which manganese is most distinctly a metallic element. The highest oxide,  $\text{Mn}_2\text{O}_7$ , is an acid anhydride.

10. **Iron, Nickel, and Cobalt.** — These elements give oxides which are feebly basic. Iron gives two extensive series of compounds in which it is bivalent and trivalent, respectively. Those of the former set resemble the bivalent salts of manganese and zinc. Those of the latter resemble the salts of aluminium. Cobalt and nickel in most of their compounds are bivalent elements, and the behavior recalls that of the compounds of bivalent manganese and zinc.

**11. Palladium and Platinum Families.** — The metals of these families have little chemical activity, and their compounds are easily decomposed by heating. Along with gold, silver, and mercury, which have similar characteristics, they are sometimes grouped together under the name of the *noble metals*.

**Occurrence of the Metals in Nature.** — The minerals from which metals are extracted are known as *ores*. They present a comparatively small number of different kinds of compounds. Most of the metals are found in more than one of these forms, so that in the following statement the same metal frequently occurs more than once.

When the metal occurs free in nature it is said to be *native*. Thus we have native gold, silver, metals of the platinum group, copper, mercury, bismuth, antimony, and arsenic (*cf.* p. 404).

The metals whose *oxides* are important minerals are iron, manganese, tin, zinc, copper, and aluminium. The metals are obtained commercially from the oxides in each of these cases.

The metals whose *sulphides* are used as ores are iron, nickel, cobalt, antimony, lead, cadmium, zinc, and copper.

From the *carbonates* we obtain iron, lead, zinc, and copper. Several other metals, such as manganese, magnesium, barium, strontium, and calcium occur in larger or smaller quantities in the same form of combination.

The metals which occur as *sulphates* are those whose sulphates are not freely soluble, namely, lead, barium, strontium, and calcium.

Compounds of metals with the *halogens* are not so numerous. Silver chloride furnishes a limited amount of silver. Sodium and potassium chlorides are found in the salt-beds, and cryolite  $3\text{NaF} \cdot \text{AlF}_3$  is used in the manufacture of aluminium.

The natural *silicates* are very numerous, but are seldom used for the preparation of the metals (see, however, zinc). Many of them are employed for other commercial purposes, kaolin (p. 636) or clay being a conspicuous example of this class.

**Methods of Extraction from the Ores.** — The art of extracting metals from their ores is called *metallurgy*. Where the metal is *native*, the process is simple, since melting away from the matrix (p. 410) is all that is required. Frequently a *flux* (p. 640) is added. A flux usually is a substance which interacts with infusible materials to give fusible ones. It combines with the matrix, giving a fusible

**slag** (resembling glass). Since the slag is a melted salt, usually a silicate, and does not mix at all with the molten metal, separation of the products is easily effected. When the ore is a *compound*, the metal has to be liberated by our furnishing a material capable of combining with the other constituent. The details of the process depend on various circumstances. Thus the volatile metals, like zinc and mercury, are driven off in the form of vapor, and secured by condensation. The involatile metals, like copper and iron, run to the bottom of the furnace and are tapped off.

Where the ore is an **oxide** it is usually reduced by heating with carbon in some form. This holds for the oxides of iron and copper, for example. Some oxides are not reducible by carbon in an ordinary furnace. Such are the oxides of calcium, strontium, barium, magnesium, aluminium, and the members of the chromium group. At the temperature of the electric furnace even these may be reduced, but the carbides are formed under such circumstances, and the metals are more easily obtained otherwise. Recently, heating the pulverized oxide with finely powdered aluminium has come into use, particularly for operations on a small scale. Iron oxide is easily reduced by this means, and even the metals manganese and chromium may be liberated from their oxides quite readily by this action. This procedure has received the name **aluminothermy** (*q.v.*), on account of the great amounts of heat liberated. In the laboratory the oxides of the less active metals are frequently reduced in a stream of hydrogen (*cf.* p. 127).

When the ore is a **carbonate**, it is first heated strongly to drive out the carbon dioxide (*cf.* p. 573):  $\text{FeCO}_3 \rightleftharpoons \text{FeO} + \text{CO}_2 \uparrow$ , and then the oxide is treated according to one of the above methods. When the ore is a **sulphide**, it has to be calcined (*cf.* p. 424) in order to remove the sulphur, and the resulting oxide is then treated as described above.

**Chlorides** and **fluorides** of the metals can be decomposed by heating with metallic sodium (*cf.* p. 630). This method was formerly employed in the making of magnesium and aluminium.

The metals which are not readily secured in any of the above ways, can be obtained easily by **electrolysis** of the fused chloride or of some other simple compound. Aluminium is now manufactured entirely by the electrolysis of a solution of aluminium oxide in molten cryolite.

**Compounds of the Metals: Oxides and Hydroxides.** — The **oxides** may be made by direct burning of the metals, by heating the

nitrates (*cf.* p. 531), the carbonates (*cf.* p. 573), or the hydroxides:  $\text{Ca(OH)}_2 \rightleftharpoons \text{CaO} + \text{H}_2\text{O}\uparrow$ . They are practically insoluble in water, although those of the metals of the alkalis and of the metals of the alkaline earths interact with water rapidly to give the hydroxides. They are usually stable. Those of gold, platinum, silver, and mercury, decompose when heated, yet with increasing difficulty in this order. The metals, like the non-metals, frequently give several different oxides. Those of the univalent metals, having the form  $\text{K}_2\text{O}$ , if we leave cuprous oxide and aurous oxide out of account, have the most strongly basic qualities. Those of the bivalent metals of the form  $\text{MgO}$ , when this is the only oxide which they furnish, are base-forming. Those of the trivalent metals of the form  $\text{Al}_2\text{O}_3$ , known as *sesquioxides* (Lat. *sesqui-*, one-half more), are the least basic of the basic oxides. The oxides of the forms  $\text{SnO}_2$ ,  $\text{Sb}_2\text{O}_5$ ,  $\text{CrO}_3$ , and  $\text{Mn}_2\text{O}_7$ , in which the metals have valences from 4 to 7, are mainly acid-forming oxides, although the same elements usually have other lower oxides, which are basic.

The **hydroxides** are formed, in the cases of the metals of the alkalis and alkaline earths by direct union of water with the oxides. They are produced also by double decomposition when a soluble hydroxide acts upon a salt (*cf.* p. 398). All hydroxides, except those of the alkali metals, lose the elements of water when heated, and the oxides remain. In some cases the loss takes place by stages, just as was the case with orthophosphoric acid (p. 558). Thus lead hydroxide  $\text{Pb(OH)}_2$  (*q.v.*) first gives the hydroxide  $\text{Pb}_2\text{O(OH)}_2$ , then  $\text{Pb}_3\text{O}_2(\text{OH})_2$ , and then the oxide  $\text{PbO}$ . The hydroxides of mercury and silver, if they are formed at all, are evidently unstable, for, when either material is dried, to remove adhering moisture, it is found to contain nothing but the corresponding oxide. With the exception of those of the metals of the alkalis and alkaline earths, all the hydroxides are little soluble in water.

**Compounds of the Metals: Salts.** — It may be said, in general, that each metal may form a salt by combination with each one of the acid radicals. In the succeeding chapters we shall describe only those salts which are manufactured commercially, or are of special interest for some other reason. The various salts will be described under each metal. Here, however, a few remarks may be made about the characteristics of the more common groups of salts. The salts are classified according to the acid radicals which they contain.

The **chlorides** may be made by the direct union of chlorine with the metal (*cf.* p. 221), or by the combined action of carbon and chlorine upon the oxide (*cf.* p. 632). The general methods for making any salt (p. 213), such as the interaction of a metal with an acid, or of the oxide, hydroxide, or another salt with an acid, or the double decomposition of two salts, may be used also for making chlorides. The chlorides are for the most part soluble in water. Silver chloride, mercurous chloride, and cuprous chloride are almost insoluble, however, and lead chloride is not very soluble. Most of the chlorides of metals dissolve without decomposition, but hydrolysis is noticeable in the case of the chlorides of the trivalent metals, such as aluminium chloride and ferric chloride (*cf.* p. 648). The chlorides of some of the bivalent metals are hydrolyzed also, but, as a rule, only when they are heated with water. This is the case with the chlorides of magnesium, calcium, and zinc. Most of the chlorides are stable when heated, but those of the noble metals, particularly gold and platinum, are decomposed, and chlorine escapes. The chlorides are usually the most volatile of the salts of a given metal, and so are preferred for the production of the spectrum (*q.v.*) of the metal, and for fixing the atomic weight of the metal by use of the vapor density. Some of the metals form two or more different chlorides. For example, indium gives  $\text{InCl}$ ,  $\text{InCl}_2$ , and  $\text{InCl}_3$ .

The **sulphides** are formed by the direct union of the metal with sulphur, or by the action of hydrogen sulphide or of some soluble sulphide upon a solution of a salt (*cf.* p. 421). In one or two cases they are made by the reduction of the sulphate with carbon. The sulphides, except those of the alkali metals, are but little soluble in water. The sulphides of aluminium and chromium are hydrolyzed completely by water, giving the insoluble hydroxides, and those of the metals of the alkaline earths are partially hydrolyzed (*cf.* p. 421).

Some of the metals, when they are in the molten form, dissolve carbon, and, when they are cooled once more, deposit it in the form of graphite. This is true particularly of platinum and iron. The **carbides** are usually formed in the electric furnace by interaction of an oxide with carbon (*cf.* p. 570). Some of them are decomposed by contact with water, after the manner of calcium carbide, giving a hydroxide and a hydrocarbon. Of this class are lithium carbide  $\text{Li}_2\text{C}_2$ , barium and strontium carbides  $\text{BaC}_2$  and  $\text{SrC}_2$ , aluminium carbide  $\text{Al}_4\text{C}_3$ , manganese carbide  $\text{MnC}$ , and the carbides of potassium and glucinum. Others, such as those of molybdenum  $\text{Mo}_2\text{C}$  and chromium  $\text{Cr}_3\text{C}_2$ , are not affected by water.

The **nitrates** may be made by any of the methods used for preparing salts. The normal nitrates are *all* at least fairly soluble in water.

The **sulphates** are made by the methods used for making salts, and in some cases by the oxidation of sulphides. They are all soluble in water, with the exception of those of lead, barium, and strontium. Calcium sulphate is meagerly soluble.

The **carbonates** are prepared by the methods used for making salts. They are all insoluble in water, with the exception of those of sodium and potassium. The hydroxides of aluminium and tin are so feebly basic and so insoluble that these metals do not form carbonates which are stable in contact with moisture (*cf.* p. 648).

The **phosphates** and **silicates** are prepared by the methods used in making salts. The former are obtained also by special processes already described (p. 559). With the exception of the salts of sodium, ammonium, and potassium, all the salts of both these classes are insoluble.

**Solubility of Bases and Salts.** — The solubilities of a few salts at various temperatures have already been given (p. 157). For the **exact solubilities** of a large number of **bases and salts** (142) at 18°, see the **Table inside the cover**, at the front of this book. Each square contains two numbers expressing the solubility of the compound whose cation stands at the head of the column and whose anion is indicated at the side. The solubility is that of the hydrate stable at 18°, where such exists. The **upper number** in each case gives the number of grams of the anhydrous salt held in solution by 100 c.c. of water. The **lower number** shows the number of moles in 1 l. of the saturated solution, and indicates therefore the concentration in terms of a molar solution as unity — the molar solubility. In the cases of the less soluble compounds the values are not exact, but they will serve to show roughly the relative solubilities when several substances are compared. The numbers for small solubilities have been abbreviated. Thus, 0.0<sub>4</sub> = 0.000004.

The following are the solubilities (number of grams in 100 c.c. water) at 18° of two additional insoluble substances and of three acid salts.

Mercurous chloride, 0.0 <sub>2</sub>	Sodium bicarbonate	9.6
(molar sol'ty, 0.0 <sub>1</sub> )	Potassium bicarbonate	26.1
Mercuric iodide, 0.0 <sub>4</sub>	Potassium bisulphate	50.0
(molar sol'ty, 0.0 <sub>1</sub> )	Sodium bisulphate (0°)	50.0

It will be seen that some compounds, like zinc chloride and barium iodide, are exceedingly soluble; that others, like potassium chloride and barium chlorate, are of medium solubility; that still others, like calcium hydroxide and calcium sulphate, are sparingly soluble; and, finally, that some, like calcium oxalate  $\text{CaC}_2\text{O}_4$  and barium chromate, are almost insoluble. The reader should note the fact, however, that the differences in solubility even amongst the insoluble salts are as great as amongst the soluble ones.

**Solubilities at different temperatures** are shown in the diagram, Fig. 79, p. 191.

**Hydrated Forms of Salts Commonly Used.** — In the table given below, the figures refer to the number of molecules of water in the hydrates which are deposited by aqueous solutions of the salts in the neighborhood of  $18^\circ$ . The letter *h* means that the compound is stable when *heated*, the letter *a* that it is not affected by the *air*, the letter *d* that the salt is *deliquescent*, and the letter *e* that the hydrate loses water spontaneously in an open vessel, *i.e.*, is *efflorescent*.

Composition of Hydrates of Salts

	K	Na	Li	Ag	Ba	Sr	Ca	Mg	Zn	Cd	Cu	Pb
Cl . . . . .	0h	0h	2a	0h	2a	6e	6d	6d	1½d	2½e	2d	0h
Br . . . . .	0h	0h	0h	0h	2a	6d	6d	6d	2d	4e	4e	0h
I . . . . .	0h	0h	0h	0h	2d	6d	0d	8d	0d	0a	..	0h
NO <sub>3</sub> . . . . .	0a	0a	0d	0a	0a	4e	4d	6d	6d	4d	6d	0a
ClO <sub>3</sub> . . . . .	0a	0a	0d	0a	1a	5d	2d	6d	6d	2d	6d	1a
BrO <sub>3</sub> . . . . .	0a	0a	0d	0a	1a	1a	1a	6e	6a	2a	6a	1a
IO <sub>3</sub> . . . . .	0a	3e	0d	0a	1a	6e	6e	4a	2a	0a	1a	0a
C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> . . . . .	0d	3e	2d	0a	1a	½a	2d	4d	3a	3d	1a	3a
SO <sub>4</sub> . . . . .	0h	10e	0h	0a	0h	0h	2a	7e	7e	2½a	5a	0h
CrO <sub>4</sub> . . . . .	0h	10e	2a	0a	0h	0h	1a	7e	..	..	..	0h
C <sub>2</sub> O <sub>4</sub> . . . . .	1a	0a	0a	0a	1a	0a	1a	2a	2a	3a	1a	0a
CO <sub>3</sub> . . . . .	1½d	10e	0a	0e	0h	0h	0a	3e	0a	0a	..	0a

**Isomorphism.** — All substances which crystallize in one of the forms belonging to the regular system (p. 172) must necessarily have identical crystalline shapes. Thus, crystallized specimens of sodium chloride and of lead sulphide (galena) in their natural shapes are cubical. The forms found in other systems, however, are capable of assuming an infinite diversity of shapes. The relative lengthening or shortening in one direction, shown by the square prismatic and hexagonal forms (p. 172), for example, makes it possible for each



separate substance to adopt proportions which are more or less different from those of every other substance. Each substance, not belonging to the regular system, does, in fact, crystallize invariably in forms based upon its own fundamental proportions, and differs therefore in its angles from all other such substances in a way that is clearly recognizable by refined measurement.

Now it is found that substances which are chemically somewhat similar (see below) frequently crystallize in the same system and show proportions which are almost, although not quite, identical. Further, two or more such substances, when the approach to identity in angles is not accidental, can take part in the construction of one and the same crystal. A crystal of one such substance placed in a solution of the other will continue to grow, and in doing so will follow the pattern already set, and simply increase in dimensions by accretion of the new material. When a solution containing two such substances deposits crystals, the structures are, not some of them of one material and some of the other, but are all made up of *both* in a ratio determined by the relative amounts of the substances in the solution.\* **Substances** related in these two ways, that is, **having, when separate, crystalline forms which are closely alike and being capable of forming homogeneous crystals containing varying proportions of the two ingredients**, are called **isomorphous substances** (Gk. *ἴσος*, equal; *μορφή*, form). Thus, potassium permanganate  $\text{KMnO}_4$  and potassium perchlorate  $\text{KClO}_4$  crystallize in the rhombic system, forming crystals with very similar angles (Fig. 70, p. 173), and when a solution containing both is allowed to evaporate there is formed but one set of crystals made up of both substances. Similarly, potassium iodide and ammonium iodide crystallize in cubes of the regular system and, since all cubes are alike, necessarily show absolutely identical angles. In addition to this, however, they crystallize together from a solution containing both salts. Other pairs from amongst substances belonging to the regular system would not do this. These two salts are therefore isomorphous. Substances which thus form mixed crystals have approximately equal molecular volumes.

In the course of our study of the compounds of the metals we shall have occasion to note many examples of isomorphism. Thus the heptahydrates of the sulphates of many of the bivalent metals, such as  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , etc., belong to the

\* In general, two substances which are absolutely unrelated may be deposited simultaneously from mixed aqueous solutions, but some of the crystals are *pure* specimens of one substance, and the rest are pure specimens of the other.

rhombic system, and form an isomorphous set of substances known as the *vitriols* (*q.v.*).

The alums (*q.v.*) also constitute an important set, and crystallize, separately and together, in the regular system. Amongst minerals, lead sulphide  $PbS$  and silver sulphide  $Ag_2S$  form a common isomorphous pair, and nearly all natural specimens of galena (*q.v.*) contain at least a little silver sulphide.

The chemical significance of isomorphism was at first exaggerated. Thus the elements magnesium and iron are not especially similar in their chemical relations, excepting that both are bivalent; yet they form several pairs of compounds which, like the sulphates (above), are isomorphous. Still, in practical chemical work a knowledge of the relations of a substance in respect to isomorphism is indispensable. It enables us to predict the probable impurities in a homogeneous-looking material, for non-isomorphous substances would have given a heterogeneous mixture with it. It assists us in separating and purifying chemical substances, for non-isomorphous substances can be separated by recrystallization from water (p. 481), or by washing with water or some other solvent (p. 484), at a temperature at which the solubilities of the substances are different (see Potassium nitrate). Isomorphous substances, however, can be separated only by conversion into some other form of combination in which the property is lacking. Thus, silver sulphide cannot be separated from lead sulphide by Pattinson's process (*q.v.*), and so the mixed metals, to the separation of which the process is applicable, must first be secured by reduction.

Some chemists regard isomorphous mixtures as solid solutions.

**Exercises.** — 1. Compare the electrical conductivities of normal sodium hydroxide and normal acetic acid with the conductivity of copper. What length of copper wire will present the same resistance as 1 cm. of each of these solutions when the cross-sections are alike?

2. What do we mean by saying that an oxide is strongly or feebly basic, or that it is acidic (p. 654)?

3. What is meant by the same terms when applied to an hydroxide?

4. Compare the molar solubilities at  $18^\circ$ , (a) of the halides of silver and (b) of the carbonates and (c) oxalates of the metals of the alkaline earths, noting the relation between solubility and atomic weight.

5. What are the molar concentrations of chloride-ion (*cf.* p. 183) in

saturated solutions of silver chloride and lead chloride at 18°, assuming complete ionization in these very dilute solutions?

6. How does the behavior of complex acids, like chloroplatinic acid  $\text{H}_2\text{PtCl}_6$ , differ from that of acid salts?

7. Formulate (p. 399) (a) the hydrolysis of ammonium orthosilicate (made by mixing solutions of ammonium chloride and sodium orthosilicate); (b) the hydrolysis of aluminium carbonate, made by mixing solutions of aluminium sulphate and sodium carbonate.

## CHAPTER XXXIII

### METALLIC ELEMENTS OF THE ALKALIES: POTASSIUM AND AMMONIUM

*The Metals of the Alkalies.* — The metals of this family form an homogeneous group, and there is a very general similarity between the properties of the corresponding compounds. Some of the physical properties of the elements themselves can best be shown in tabular form.

	At. Wt.	Sp. Gr.	M.-P.	B.-P.
Lithium Li . . . . .	6.94	0.53	186°	above red heat.
Sodium Na . . . . .	23.00	0.97	95.6°	742°
Potassium K . . . . .	39.10	0.86	62.5°	720°
Rubidium Rb . . . . .	85.45	1.53	38.5°	.....
Caesium Cs . . . . .	132.81	1.87	28.5°	270°

It will be seen that the specific gravities of the elements increase with rising atomic weight, while the melting-points and boiling-points fall (*cf.* p. 462). A table including all the physical properties, both of the elements and their compounds, would show similar characteristics in a general way, with here and there noticeable irregularities such as that shown by the specific gravity of sodium. For example, the melting-points of the hydroxides are: sodium 318.4°, potassium 360.4°, rubidium 301°, caesium 272.3°. Sodium (m.-p. 95.6°) and potassium (m.-p. 62.5°) give together an alloy which is *liquid* at room temperature (p. 644).

*The Chemical Relations of the Metallic Elements of the Alkalies.* — The metals which are chemically most active are included in this group, and the activity increases with rising atomic weight, caesium being the most active positive element of all. A freshly cut surface of any of these metals tarnishes by oxidation as soon as it is exposed to the air. Indeed, there is scarcely time to see the metallic appearance in the case of potassium and the metals following it. All of these metals decompose water violently (*cf.* p. 115),

liberating hydrogen. The hydroxides which are formed by this action are exceedingly active bases, that is to say, they give a relatively large concentration of hydroxide-ion in solutions of a given molecular concentration (p. 374). Lithium hydroxide is the least active. In the dry form these hydroxides are not decomposed by heating, while the hydroxides of all other metals lose water more or less easily. All these metals seem to combine with hydrogen, lithium giving the most stable compound. The hydrides, however, unlike those of many of the non-metals, are not ionogens, and consequently do not give acids when dissolved in water. In all their compounds the metals of the alkalis are univalent.

The family may be subdivided into two minor groups. The compounds of potassium, rubidium, and caesium resemble one another closely, while those of sodium and lithium are sometimes largely divergent in physical properties. Thus, the chlorides of the potassium set, not only crystallize in cubes, but can form mixed crystals with one another in all proportions. They are isomorphous (*cf.* p. 658). The same is true of the bromides and of the iodides. Sodium chloride, although crystallizing in cubes likewise, does not form mixed crystals with the chlorides of the potassium set. In the case of lithium, the hydroxide is not nearly so soluble as are the hydroxides of the other metals, and the metal gives also an insoluble carbonate and phosphate, in which respect it resembles magnesium and differs from all the other members of the present group.

The compounds of ammonium will be discussed in connection with those of potassium, to which they present the greatest resemblance.

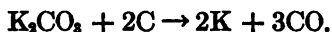
The solubilities are often decisive factors in connection with the preparation and use of salts. The reader will find most of these in the Table inside the front cover, or in the diagram on p. 191, and, as a rule, the values will not be repeated in the descriptive paragraphs.

### POTASSIUM K

**Occurrence.** — Silicates containing potassium, such as felspar and mica (p. 636), are constant constituents of volcanic rocks, and from the weathering of these rocks, and of the detritus formed from them which constitutes a large part of the soil, the potassium used by plants is obtained. These minerals are not used commercially as sources of potassium compounds. The salt deposits (see below) contain potassium chloride, alone (sylvite) and in combination with other salts, and most of the compounds of potassium are manufactured

from this material. Part of our potassium nitrate, however, is purified Bengal saltpeter (p. 525). Potassium sulphate occurs also in the salt layers, and is used directly as a fertilizer.

**Preparation.** — Potassium was first made by Davy (1807) by bringing the wires from a battery in contact with a piece of moist potassium hydroxide. Globules of the metal appeared at the negative wire. This process has again come into use, commercially, molten potassium chloride being the substance decomposed. The process which, during the intervening years, furnished potassium, was the heating of potassium carbonate with finely divided carbon in small retorts:



The vapor of the metal tends to combine with the carbon monoxide, forming an explosive compound  $\text{K}_2\text{C}_2\text{O}_2$ , and the yield is thus reduced.

**Physical Properties.** — Potassium is a silver-white metal which melts at  $62.5^\circ$ . It boils at  $720^\circ$ , giving a greenish vapor. The metal and its compounds confer a violet tint upon the Bunsen flame, and the spectrum (*q.v.*) shows characteristic lines.

**Chemical Properties.** — The density of the vapor shows the molecular weight of potassium to be about 40, so that the vapor is a monatomic gas. The element unites violently with the halogens, sulphur, and oxygen. In consequence of the latter fact it is usually kept under petroleum, an oil which neither contains oxygen itself, nor dissolves a sufficient amount of moisture from the air (*cf.* p. 87) to permit much oxidation of the potassium to take place.

**The Hydride KH.** — When hydrogen is passed over potassium heated to  $360^\circ$ , a hydride is formed. By washing the solid product with liquefied, dry ammonia the excess of potassium is removed and white crystals remain. These have the composition KH. On account of the ease with which it decomposes, the substance behaves much like potassium itself. When thrown into water, for example, it gives potassium hydroxide, and the hydrogen is liberated (*cf.* p. 703).

**Potassium Chloride KCl.** — Sea-water and the waters of salt lakes contain a relatively small proportion of potassium compounds. During the evaporation of such waters, however, the potassium com-

pounds tend to accumulate in the mother-liquor while sodium chloride is being deposited. Thus, when the Salt Lake in Utah shall have finally dried up, the *upper* (last to be formed) part of the bed of salts which it will leave behind will contain layers rich in compounds of potassium. This condition is realized in geological deposits which have been formed in the same way. Thus, at Stassfurt, near Magdeburg, there is a thickness of more than a thousand meters of common salt, more or less mixed with and intersected by layers of sedimentary deposits. Above this, and therefore deposited last, are 25–30 meters of salt layers in which the potassium salts are chiefly found, while over all are several hundred meters of sandstone. Formerly the upper layers were simply stripped off and rejected. Now, however, the revenue obtained from the products of these layers is many times greater than that coming from the rock salt below.

The forms in which the potassium chloride is found in the salt beds are sylvite  $\text{KCl}$  and carnallite  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . The latter is heated with a small amount of water, or with a mother-liquor obtained from a previous operation and containing sodium and magnesium chlorides. The magnesium sulphate which it contains as an impurity remains undissolved. From the clear liquid, when it cools, potassium chloride is deposited first and then carnallite. The former is taken out and purified, and the latter goes through the process again. This potassium chloride is the source from which most of our potassium hydroxide and potassium carbonate, as well as salts of minor commercial importance, are made. It is a white substance crystallizing in cubes, melting at about  $750^\circ$ , and slightly volatile at high temperatures.

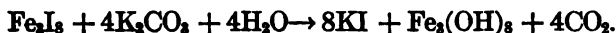
Recently, the giant kelps of the Pacific coast have been used as a source of potassium chloride. The dried seaweed contains 9 per cent of this salt and about 0.1 per cent of iodine.

**Potassium Iodide  $\text{KI}$ .**—When iodine is heated in a solution of potassium hydroxide, the iodate and iodide are both formed (p. 487):



The dry residue from evaporation is heated with powdered carbon to reduce the iodate, and all the iodide can then be purified by recrystallization. Another method of preparation consists in rubbing together iodine and iron filings under water. The soluble ferrous iodide  $\text{FeI}_2$ , thus formed is then treated with additional iodine and gives a substance  $\text{Fe}_3\text{I}_8$ , intermediate in composition between ferrous and ferric

iodides. This is also soluble. When potassium carbonate is added to the solution, a hydrated magnetic oxide of iron is precipitated, carbon dioxide escapes, and evaporation gives potassium iodide:



The salt forms large, somewhat opaque cubes (m.-p.  $623^\circ$ ). It is used in medicine and for precipitating silver iodide  $\text{AgI}$  in photography. In the laboratory it is used whenever an iodide is required, for example, when experiments with iodide-ion are to be made.

The aqueous solution takes up free iodine, forming  $\text{KI}_3$ , in equilibrium with dissolved iodine:  $\text{I}_3^- \rightleftharpoons \text{I}^- + \text{I}_2$  (dissolved). The mixture is used in testing for starch, and in reactions in which a solution of free iodine is required.

**The Bromide and Fluorides.** — Potassium bromide  $\text{KBr}$  may be made in either of the ways used for the iodide. It crystallizes in cubes. It is used in medicine and for precipitating silver bromide in making photographic plates (*q.v.*). In the laboratory it is always employed when a bromide is needed as a source of bromide-ion.

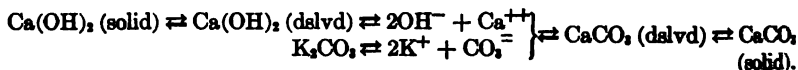
The fluoride of potassium  $\text{K}_2\text{F}_2$  may be obtained by treating the carbonate or hydroxide with hydrofluoric acid. It is a deliquescent, white salt. When treated with an equi-molecular quantity of hydrofluoric acid it forms potassium-hydrogen fluoride  $\text{KHF}_2$ , a white salt which is also very soluble. This acid salt is used in the preparation of pure hydrofluoric acid, since the latter is liberated from it as a vapor at a high temperature.

Potassium chloride is the least soluble of the halides of potassium, the bromide, fluoride, and iodide coming next in that order. The position of the fluoride as the third in order, when we should expect it to be the least soluble (p. 284), shows that this compound is somewhat exceptional. It is also slightly hydrolyzed by water, as if it were a salt of a dibasic acid (*cf.* p. 439). These facts, together with the existence of the acid fluoride, lead us to assign to it the formula  $\text{K}_2\text{F}_2$ . Other acid fluorides of the formulæ  $\text{KH}_2\text{F}_3$  and  $\text{KH}_2\text{F}_4$  have likewise been made. Since potassium, hydrogen, and fluorine are always univalent, and no ordinary valence is thus available for holding together groupings more complex than  $\text{KF}$  and  $\text{HF}$ , we may regard all these four fluorides of potassium as molecular compounds (p. 530).

**Potassium Hydroxide  $\text{KOH}$ .** — This compound, known also as caustic potash and colloquially as potassium hydrate (p. 150), was



formerly made entirely by boiling potassium carbonate with calcium hydroxide suspended in water (milk of lime):



The operation is conducted in iron vessels, because porcelain, being composed of silicates, interacts with solutions of bases. The action is, in theory, precisely similar to that of sulphuric acid upon barium dioxide (*cf.* p. 317). The potassium carbonate corresponds to the acid, being completely dissolved from the beginning, and the calcium hydroxide to the dioxide, since its relative insolubility (0.17 g. in 100 g. Aq) enables the water to take up fresh portions into solution only when the part dissolved has already undergone chemical change. The calcium carbonate which is precipitated is still more insoluble (0.0013 g. in 100 g. Aq) than the hydroxide, and hence the action goes forward. The action as a whole is reversible, for a reason which will be explained later (p. 700), and consequently such an amount of water is employed that the solution at no time contains more than about ten per cent of potassium hydroxide (sp. gr. 1.1). The conclusion of the action is recognized when a clear sample of the liquid no longer effervesces on addition of a dilute acid, and is therefore free from potassium carbonate. After the precipitate has settled, the potassium hydroxide is obtained by evaporation of the clear liquid,  $\text{K}^+ + \text{OH}^- \rightarrow \text{KOH}$ .

Potassium hydroxide is now manufactured by **electrolytic processes**. When a solution of potassium chloride is electrolyzed, chlorine is liberated at the anode, and hydrogen and potassium hydroxide at the cathode. The necessity of keeping those two sets of products apart, since by their interaction potassium hypochlorite and potassium chloride would be formed (*cf.* p. 475), has made the devising of suitable apparatus extremely difficult. In one type of apparatus a partition of asbestos cloth divides the cell into two parts. In some cases this is placed vertically, and in others horizontally. In the latter case the anode is on the upper side of the partition, in order that the chlorine as it is liberated may ascend to the surface without stirring up the liquid or having occasion to pass near the partition. In all cases the anode is made of graphite, since this substance is less easily attacked by chlorine than is any other, and the cathode is made of iron, a metal which best resists the action of alkalis. The chlorine is used for making bleaching powder. Pure brine flows in continuously at one point, and a solution of the hydroxide containing much undecom-

posed chloride flows out at another. The **Townsend-Baekeland, Briggs, and Du Bois** cells are of this type.

The same process is applied to sodium chloride. In both cases, the chlorine is compressed in iron cylinders to give liquid chlorine (*cf.* p. 221) or is used to prepare hypochlorites such as bleaching powder. The hydrogen, in some cases, is also utilized. It should be noted that in the electrolysis of solutions of potassium chloride or sodium chloride, **potassium or sodium is not set free**. The salts are highly ionized, and their ions carry the current efficiently by migration between the electrodes. But, when potassium-ion reaches the cathode, there is a choice between discharging either the  $K^+$ , or the  $H^+$  of the water. The latter is much more easily discharged (see Chap. XXXVIII), and **so hydrogen is liberated**. There is not nearly so much hydrogen-ion present at any one time as there is potassium-ion, but, as the  $H^+$  is discharged and removed, the instantaneous ionization of more water restores the supply.

The **Castner-Kellner apparatus** (Fig. 140) employs a different principle very ingeniously for the separation of the products. The two end compartments are filled with brine and contain the graphite

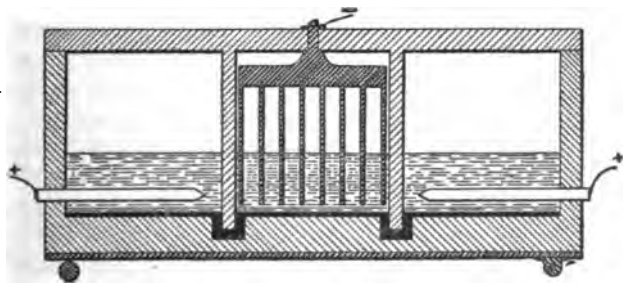


FIG. 140.

**anodes.** The central compartment contains potassium (or sodium) hydroxide solution and the iron cathode. The positive current enters by the anodes, and the chlorine is therefore attracted to and liberated upon the graphite:  $2Cl^- + 2\oplus \rightarrow Cl_2\uparrow$ . After rising through the liquid it is collected for the manufacture of liquefied chlorine or of bleaching powder. The ions of potassium or of sodium, as the case may be, are discharged upon a layer of mercury which covers the whole floor of the box, and the free metal dissolves in the mercury, forming an amalgam (p. 644). The *dilution* of the sodium by mercury permits the discharge of the sodium-ion, making this discharge

easier than that of hydrogen-ion. The layer of mercury extends beneath the partitions, and a slight rocking motion given to the cell by the cam causes the amalgam to flow below the partition into the central compartment. Here the sodium leaves the mercury in the form of sodium ions and is attracted by the cathode. Upon this, hydrogen from the water ( $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$ ) is discharged, and the residual hydroxide-ion, together with the metal-ion, constitutes potassium or sodium hydroxide:  $2\text{K}^+ + 2\text{OH}^- + 2\text{H}^+ + 2\ominus \rightarrow 2\text{K}^+ + 2\text{OH}^- + \text{H}_2 \uparrow$ . A slow influx of salt solution at one point and overflow of the alkaline solution in the central cell at another, is maintained. The overflowing liquid contains 20 per cent of alkali. Since in this form of the apparatus there is no undecomposed chloride present in the part of the solution which contains the hydroxide, simple evaporation to dryness furnishes the solid alkali. The amount of mercury required, however, involves a large investment of capital.

Potassium hydroxide is exceedingly soluble in water, and consequently, instead of being crystallized from solution, the molten residue from evaporation is cast in sticks. When, for chemical purposes, the hydroxide is required free from potassium carbonate and other impurities, it is dissolved in alcohol, in which the other substances are not soluble. Evaporation of this solution gives pure caustic potash. The hydroxide, because of its great solubility and the consequent very low vapor tension of its solution (cf. p. 197), is highly deliquescent. It also absorbs carbon dioxide from the air, giving potassium carbonate. This salt is itself deliquescent, and consequently a syrupy solution of the carbonate is the final result of weathering. Solutions of the hydroxide have an exceedingly corrosive action upon the flesh, decomposing it into a slimy mass by hydrolyzing the proteins, which are easily decomposed into organic acids. In solution, the base is highly ionized, furnishing a high concentration of hydroxide-ion. Its aqueous solution is therefore used with salts of other metals for precipitation of less soluble bases.

**The Oxides.** — The simple oxide  $\text{K}_2\text{O}$  may be made by heating potassium nitrate or nitrite with potassium in a vessel from which air is excluded:  $2\text{KNO}_3 + 10\text{K} \rightarrow 6\text{K}_2\text{O} + \text{N}_2$ . It interacts violently with water, giving the hydroxide. When exposed to the air it unites spontaneously with oxygen, and a yellow peroxide  $\text{K}_2\text{O}_4$  is formed.

When the metal burns in oxygen,  $\text{K}_2\text{O}_4$ , a yellow solid is the product. This substance interacts violently with water, giving potassium

hydroxide, and the excess of oxygen is liberated. With perfectly dry oxygen, potassium does not unite, even when it is heated strongly.

**Potassium Chlorate  $KClO_3$ .** — The preparation of this salt, by interaction of potassium chloride with calcium chlorate, has already been described (p. 481). It is also made by electrolysis of potassium chloride solution, the potassium hydroxide and chlorine which are liberated being precisely the materials required. All that is necessary is to use a warm, concentrated solution and to provide for the mixing of the materials generated at the electrodes. The salt crystallizes out when the solution cools.

Potassium chlorate crystallizes in monoclinic plates. It melts at about  $351^\circ$ , and at a temperature slightly above this the visible liberation of oxygen begins. Since heat is given out by the decomposition, the action may be almost explosive if large amounts of the material are employed. On account of the ease with which its oxygen is liberated, the salt is employed in making fireworks and as a component, along with antimony trisulphide, of the heads of Swedish matches. With acids it is used as an oxidizing agent on account of the chloric acid which is set free (p. 480). It is also employed in medicine as a gargle.

**Potassium perchlorate  $KClO_4$ ,** formed by the heating of the chlorate (p. 483), gives white crystals belonging to the rhombic system. Compared with the chlorate, on account of the greater difficulty in liberating its oxygen by heat, it finds little practical application.

By adding chlorine-water to potassium carbonate solution, a mixture of the chloride and **potassium hypochlorite** is formed:



The carbonic acid, however, is not completely displaced by the  $HClO$ , which is a feeble acid, and so some  $HClO$  remains. Hence, the solution is used, under the name *eau de Javel* (often misspelt *Javelle*), in the household for removing stains.

**The Bromate and Iodate.** — These are the most familiar salts of their respective acids. The mode of their preparation has already been described (p. 487). Potassium iodate  $KIO_3$  may be made also very conveniently by melting together potassium chlorate and potassium iodide at a low temperature. The iodate is much less soluble than the chloride, and the mixture may be separated by crystallization from water.

**Potassium Nitrate  $KNO_3$ .**—The formation of this salt in nature and its mode of extraction and purification have already been described (p. 525). This source of supply proved insufficient, for the first time, during the Crimean war (1852–55), and a method of manufacture from Chile saltpeter (sodium nitrate), which is a much cheaper substance, was introduced. Sodium nitrate and potassium chloride are heated with very little water, and the sodium chloride produced by the action, which is a reversible one, is by far the least soluble of the four salts (see diagram, p. 191). On the other hand, in hot water, the potassium nitrate is by far the most soluble. Hence the hot liquid drained from the crystals contains the required salt, and much of the sodium chloride is in the form of a precipitate. If the solubility curve of potassium nitrate (p. 191) is examined, it will be seen that this salt is but slightly soluble in cold water, and hence most of it is deposited when the solution cools. The crystals are mixed with little sodium chloride, for, as the curve shows, common salt is little less soluble at  $10^\circ$  than it is at  $100^\circ$ .

Potassium nitrate gives long prisms belonging to the rhombic system (Fig. 71, p. 173). It melts at about  $339^\circ$ , and when more strongly heated gives off oxygen, leaving potassium nitrite  $KNO_2$  (p. 537). Although it does not form a hydrate, the crystals enclose small portions of the mother-liquor, and consequently contain both water and impurities. When heated, the crystals fly to pieces explosively (*decrepitate*), on account of the vaporization of this water. Many substances which form large crystals, and do not melt when warmed, behave in the same way and for the same reason. In consequence of this, the purest salt is made by violent stirring of the solution during the operation of crystallization, the result being the formation of a crystal-meal.

Potassium nitrate is used chiefly in the manufacture of **gunpowder**, which contains 75 per cent of the highly purified salt. The other components are 10 per cent of sulphur, 14 per cent of charcoal, and about 1 per cent of water. The ingredients are intimately mixed in the form of paste, and the material when dry is broken up and sifted, grains of different sizes being used for different purposes. The chemical action which takes place when gunpowder is fired in an open space probably results chiefly in the formation of potassium sulphide, carbon dioxide, and nitrogen:



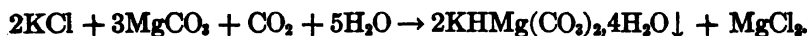
The explosion occurring in firearms follows a much more complex

course, and half of the solid product is said to be potassium carbonate (a solid, hence the smoke). One gram yields 264 c.c. of gases (0° and 760 mm.), and a much larger volume at the temperature of the explosion, and gives 660 calories. The pressure, at the temperature of the explosion, if the gases could be confined within the volume originally occupied by the gunpowder, would reach about forty-four tons per square inch. In recent years common gunpowder has been displaced largely by **smokeless powder** (pp. 528, 541), which, in decomposing, produces no solids.

Potassium nitrate is used also in preserving ham and corned beef, on which it confers a red color.

Paper saturated with potassium nitrate solution and dried, is known as **touch-paper**. The salt interferes with the access of air to the cellulose, and the oxygen for the combustion is obtained from the nitrate. The product consequently does not blaze, yet cannot be blown out.

**Potassium Carbonate  $K_2CO_3$ .**—This salt is manufactured from potassium chloride, which is heated with magnesium carbonate (magnesite), water, and carbon dioxide under pressure:



The hydrated mixed salt is separated from the liquid containing magnesium chloride and decomposed by heating with water at 120°. The product is a solution of potassium carbonate, from which the precipitated magnesium carbonate is removed by filtration and used again. A certain amount is also obtained from the fatty material, known as *suint*, which forms about 50 per cent of the weight of sheep's wool. The suint is separated from the latter by washing. When this material, which contains the potassium salt of sudoric acid in large proportions, is calcined, potassium carbonate remains, and is extracted from the ash with water. Some plants, like the sugar-beet, take up exceptional quantities of potassium salts from the soil. The molasses remaining from the crystallization of beet-sugar (p. 606) is mixed with yeast and fermented. After the alcohol has been distilled off, the liquid, containing organic salts of potassium in solution, is evaporated, and the residue is ignited. In some districts potassium carbonate is still extracted from wood-ashes, its original source and the origin of its name, **potash**.

This salt is usually sold in the form of an anhydrous powder (m.-p. over 1000°). When crystallized from water it gives a hydrate  $2K_2CO_3 \cdot$

$3\text{H}_2\text{O}$ . It is extremely deliquescent. Its aqueous solution has an alkaline reaction. The hydrolysis of the salt by the water is exactly analogous to that of sodium sulphide (p. 418), although much slighter. The more elaborate scheme given in that connection may be put in simpler form to show that the action consists essentially in the formation of the ion  $\text{HCO}_3^-$ , by union of the ion  $\text{CO}_3^{=}$  with the  $\text{H}^+$  of the water. This takes place because the ionization of the  $\text{HCO}_3^-$  ion is small enough to be commensurable with that of water itself:  $\text{CO}_3^{=} + \text{H}^+ + \text{OH}^- \rightarrow \text{HCO}_3^- + \text{OH}^-$ . The commercial name of the substance is **pearl ash**. It is used in making soft soap and hard (infusible) glass. It is also employed, by interaction with acids, in making salts of potassium.

The use of the **bicarbonate**  $\text{KHCO}_3$  in purifying carbon dioxide has already been mentioned (p. 573). Before the nineteenth century, this salt was used under the name **saleratus** (Lat. *aerated salt*), a name now sometimes given to the baking soda  $\text{NaHCO}_3$ , which has displaced it.

When a concentrated solution of the salt is electrolyzed in such a way that the anode, towards which the  $\text{KCO}_3^-$  ions travel, consists of a thin platinum wire, the crowding together of the discharged material results in the formation of the **percarbonate** (cf. p. 449):



The operation must be conducted between  $-15^\circ$  and  $0^\circ$ . When the solution in the porous cell surrounding the anode is evaporated, the product is obtained as an amorphous bluish-white powder. The substance liberates oxygen when heated, and in other respects behaves like the persulphates. When it is treated with a dilute acid, a solution containing hydrogen peroxide is formed. The compound is therefore a mixed anhydride (p. 449) of hydrogen peroxide and potassium bicarbonate.

**Potassium Cyanide.** — Formerly this compound was made by heating potassium carbonate with nitrogenous animal matter. So many other substances were formed at the same time, however, that the required product, which is very soluble, was difficult to isolate in a state of purity. It is now made by heating together potassium ferrocyanide (*q.v.*) with sodium:  $\text{K}_4\text{Fe}(\text{CN})_6 + 2\text{Na} \rightarrow 4\text{KNC} + 2\text{NaNC} + \text{Fe}$ , which gives a mixture of both cyanides. When the residue is extracted with water, only the cyanides dissolve, and are easily crystallized in pure form from the solution. Very interesting.

is the formation of potassium cyanide in the blast furnace (*q.v.*). Carbon and nitrogen unite at a very high temperature to form cyanogen (p. 625), which is an endothermal compound (van't Hoff's law, p. 305), and a sufficient amount of potassium is found in the materials to complete the production of the salt.

Potassium cyanide crystallizes in cubes. It is extremely soluble in water, and is therefore deliquescent. Its poisonous qualities are equal to those of hydrocyanic acid. The acid is so feeble as to be liberated even by the carbon dioxide of the air, and hence this salt always has a distinct odor of hydrocyanic acid. Potassium cyanide has a great tendency to form complex compounds with cyanides of other metals (*cf.* p. 649). Complex compounds of this kind were used in the galvanic deposition of silver and gold in commercial electroplating, and were formed when the cyanide was used in extracting gold (*q.v.*) from its ores. For these purposes, sodium cyanide, which is now much cheaper, has entirely displaced the potassium salt. The tendency to form complex compounds is doubtless connected with the fact that the cyanides are unsaturated compounds in which the carbon has two free valences:  $K - N \equiv C$  (p. 626).

Potassium cyanate  $KNCO$  is made by heating potassium cyanide in the air, or, still better, with some easily decomposed oxide (p. 626). It is a white, easily soluble, crystalline salt.

Potassium thiocyanate  $KNCS$  may be obtained by melting potassium cyanide with sulphur (*cf.* p. 626). It is a white, deliquescent salt which finds some applications in chemical analysis.

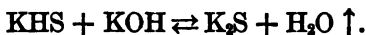
**The Sulphate and Bisulphate.**—The sulphate of potassium is a constituent of several double salts found in the Stassfurt deposits. It is extracted from *schoenite*  $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$  and *kainite*  $MgSO_4 \cdot MgCl_2 \cdot K_2SO_4 \cdot 6H_2O$ . The former is treated with potassium chloride and comparatively little water, whereupon the relatively insoluble potassium sulphate crystallizes out, and the magnesium chloride remains in the mother-liquor. The crystals belong to the rhombic system, contain no water of crystallization, and melt at  $1066^\circ$ . This salt is employed in making potassium carbonate by the Le Blanc process and in preparing alum (*q.v.*). It is also much used as a fertilizer. Since plants take up solutions through their cell walls, they can absorb soluble compounds only. They are, therefore, dependent, for the potassium compounds which they require, upon the weathering out of soluble potassium compounds from the insoluble potassium silicates contained in the soil. The weathering takes place too slowly



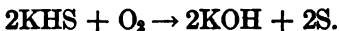
to furnish a sufficient supply for many crops, particularly that of the sugar-beet. Hence potassium sulphate is mixed directly with the soil. The mineral kainite itself is used for the same purpose.

**Potassium-hydrogen sulphate** (bisulphate)  $\text{KHSO}_4$  is made by the action of sulphuric acid upon potassium sulphate:  $\text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \rightarrow 2\text{KHSO}_4$ . It crystallizes from water, in which it is very soluble, in tabular crystals. When heated to about  $200^\circ$  it melts, and the elements of water are eliminated, the **pyrosulphate** remaining:  $2\text{KHSO}_4 \rightarrow \text{H}_2\text{O} + \text{K}_2\text{S}_2\text{O}_7$ . The latter, when still further heated, yields sulphur trioxide and potassium sulphate. The bisulphate is used in analysis for the purpose of interacting with oxides and silicates and converting them into sulphates. The substance is more efficient than sulphuric acid for this purpose, because the latter cannot be heated above  $330^\circ$ , while the liberation of the active sulphur trioxide from this salt takes place at a bright-red heat. The aqueous solution of the bisulphate is strongly acid on account of the considerable ionization of the hydrosulphate-ion.

**Sulphides of Potassium.**—By the treatment of a solution of potassium hydroxide with *excess* of hydrogen sulphide, a solution of **potassium-hydrogen sulphide** is obtained. Evaporation of the solution gives a deliquescent solid hydrate  $2\text{KHS}, \text{H}_2\text{O}$ . When the solution, before evaporation, is treated with an equivalent amount of potassium hydroxide, and the water is driven off, the **sulphide**  $\text{K}_2\text{S}$  remains behind (*cf.* p. 418):



With proper care, the very soluble hydrate  $\text{K}_2\text{S}, 5\text{H}_2\text{O}$  may be obtained. Considerable amounts of sulphur can be dissolved in solutions of either of these sulphides. By evaporation of the resulting yellow liquids, various **polysulphides** have been obtained. To some of these have been ascribed the formulæ  $\text{K}_2\text{S}_3$ ,  $\text{K}_4\text{S}_7$ ,  $\text{K}_2\text{S}_4$ ,  $\text{K}_4\text{S}_8$ , and  $\text{K}_2\text{S}_6$ , but they are probably  $\text{K}_2\text{S}_5$  (which has been isolated), or mixtures of the pentasulphide with  $\text{K}_2\text{S}$ . Similar substances are produced, as a result of the liberation and recombination of sulphur, when the solutions are exposed to the oxidizing action of the air:



In most respects the corresponding compounds of potassium and sodium are similar in their physical properties and chemical action. Since, however, the latter are almost uniformly less expensive, they

find much wider application. In a few cases, however, the potassium salt is more generally used. Thus, potassium chlorate and potassium iodide are much less soluble than the corresponding sodium compounds, and it is consequently possible in each of these two cases to separate by crystallization, and to purify the potassium salt with greater ease.

**Properties of Potassium-ion  $K^+$ : Analytical Reactions.** —

The positive ionic material of the potassium salts is a colorless substance. It unites with all negative ions, and most of the resulting compounds are fairly soluble. For its **recognition** we add solutions containing those ions which give with it the least soluble salts. Thus, with chloroplatinic acid  $H_2PtCl_6$  it gives a yellow precipitate of potassium chloroplatinate  $K_2PtCl_6$ . Since nearly one part of this salt dissolves in 100 parts of water, the test is far from being a delicate one. The solubility in alcohol is much smaller, and consequently the precipitate may frequently be obtained from a dilute solution by adding more than an equal volume of alcohol. Picric acid (p. 527) gives potassium picrate  $KOC_6H_2(NO_2)_3$ , which is much less soluble in water (0.4 parts in 100 at  $15^\circ$ ). Perchloric acid  $HClO_4$  and hydrofluosilicic acid  $H_2SiF_6$  likewise give somewhat insoluble salts of potassium. **Potassium-hydrogen tartrate**  $KHC_4H_4O_6$  is precipitated by the addition of tartaric acid to a sufficiently concentrated solution of a potassium salt. The normal tartrate  $K_2C_4H_4O_6$  is much more soluble. It may be obtained by treating the precipitate with a solution of potassium hydroxide. Addition of an acid to this solution causes reprecipitation of the bitartrate.

**The Spectroscope.** — A much more delicate test for the recognition of a potassium compound consists in the examination by means of the spectroscope of the light given out by a Bunsen flame, in which a little of the salt is held upon a platinum wire. When the amount of potassium is considerable, and no other substance which would likewise color the flame is present to mask the effect, the violet tint is recognizable by the eye. In general, however, the light must be analyzed.

White light is composed of vibrations of every wave-length within a certain range. If the light is made up of a few wave-lengths only, it appears to the eye to be colored. Now, when a narrow bundle of rays of white light, coming through a slit, falls upon a three-sided prism standing with its edges parallel to the slit, the rays of various

wave-lengths are retarded to different extents as they pass through the glass, and in consequence are bent from their paths by varying amounts. Fig. 141 shows a horizontal section through the slit (*S*) and prism, in which the width of the slit and of the beam of light are

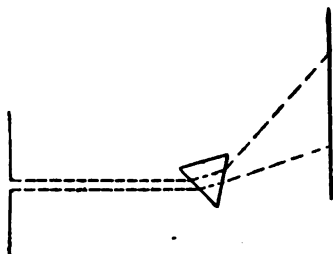


FIG. 141.

exaggerated. The light emerging at the other side of the prism consists, therefore, of a series of images of the slit arranged side by side. The red light is least refracted, and the red images of the slit, therefore, are most nearly in the same straight line with the original beam. The yellow, green, blue, and violet images are displaced more and more from this direction, and the resulting colored band is called a

**spectrum.** The whole series of images of the slit may be received upon a screen, or directly upon an eye looking towards the prism. Now, when the light comes from the vapor of potassium heated in a Bunsen flame, there are produced, not thousands of images of the slit, representing as many different wave-lengths of light, but only two images, one red, and one deep blue, corresponding to the two wave-lengths which are alone contained in the original light. In a more powerful instrument other fainter lines are seen also. Naturally the brightness of all these lines is together equal to that of the original beam. No other substance gives any of those particular lines, although many others give blue and red light of somewhat different wave-lengths. Thus, strontium compounds give a blue light along with several red tints, but when strontium and potassium are used together, the lines are found not to be coincident. In the case of strontium, all the lines lie nearer to the yellow than in that of potassium. Since the whole light of the compound is thus concentrated in one or two narrow strips, easily visible against a dark background, small amounts of the elements give effects which are readily recognizable in the instrument. This remains true even when, to the eye, the colors are completely obscured by the much more brilliant, yellow light which compounds of sodium produce. In the spectrum of sodium, this yellow light is all concentrated into two yellow lines which lie very close together.

Helium gives many lines, but one orange line ( $D_3$ ), in particular, was noted in the spectrum of the sun's photosphere many years before the element was obtained from terrestrial sources by Ramsay. When

the spectra of helium and other gases are to be examined in the laboratory, a little of the material is enclosed in a narrow, exhausted tube, through which an electrical discharge can be passed between platinum wires. Under this treatment helium shows its conspicuous orange line, and hydrogen a red and two blue ones. In this apparatus compounds are dissociated and give the spectra of their constituents. When a Bunsen flame is used with the salts\* of metals, however, the temperature is not high enough to render visible the spectra of the non-metals contained in them. Indeed, even of the metals themselves, only the members of the alkali and alkaline-earth groups give distinct results.

### RUBIDIUM AND CAESIUM

Soon after the invention of the spectroscope by Bunsen and Kirchhoff, the instrument was applied to the examination of many substances. In 1860 Bunsen discovered several new lines in the spectrum given by materials derived from the salts in Dürkheim mineral water. Two new elements of the alkali group were found to cause their presence, and were named, from the colors of the lines which they gave, rubidium (red) and caesium (blue). Both elements have since been found in small quantities in various minerals. Rubidium is obtainable with relative ease from the mother-liquors of the Stassfurt works.

The metals may be obtained by heating their hydroxides with magnesium powder. The salts of these two elements are, in crystalline form and solubility, very much like those of potassium. In some cases the difference in solubility is sufficient to make separation possible. Thus, a mixture containing compounds of these two metals and of potassium gives with chloroplatinic acid a yellow precipitate, consisting of the three insoluble chloroplatinates. The solubilities at 10°, however, are as follows: Potassium chloroplatinate 0.9, rubidium chloroplatinate 0.15, caesium chloroplatinate 0.05. Hence, when the mixed precipitates are carefully washed with small quantities of cold water the potassium chloroplatinate can be almost entirely removed. On similar principles the two other metals can be separated from one another. The iodides of all three elements combine with iodine, giving tri-iodides (*cf.* p. 665), of which the tri-iodide of caesium is the most stable. The extra iodine must be held to have entered into

\* The chlorides are preferred because of their volatility. The salts of the oxygen acids are dissociated, and leave the highly involatile oxides (*e.g.*, pp. 430, 531).

combination with the iodine of the compound, and not with the metal. In the parallel case of hydriodic acid, the union with extra iodine (p. 279) seems to show conclusively that iodide-ion can combine with iodine. While an inclination to trivalence in one of the metals of the alkalis would furnish a very acceptable link between the two sides of the first column in the periodic table (p. 466), since gold is a trivalent element, no such tendency has been proven.

### AMMONIUM

The compounds of ammonium claim a place with those of the alkali metals because in aqueous solution they give ammonium-ion  $\text{NH}_4^+$ , an ion which in its behavior closely resembles potassium-ion. Some of the special properties peculiar to ammonium compounds, and particularly the properties of ammonium hydroxide  $\text{NH}_4\text{OH}$ , have been discussed in detail already (pp. 519-521).

**Ammonium Chloride  $\text{NH}_4\text{Cl}$ .**— This salt, known commercially as *sal ammoniac*, like all the other compounds of ammonium, is prepared from the ammonia dissolved by the water used to wash illuminating-gas (p. 613). It is purified by sublimation, and then forms a compact fibrous mass. It crystallizes from solution in forms of the regular system, which are often arranged according to a feathery pattern. At  $337.8^\circ$  its vapor exercises one atmosphere pressure, and is dissociated into ammonia and hydrogen chloride to the extent of 62 per cent (p. 520).

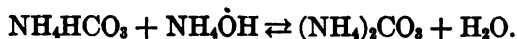
**Ammonium bromide  $\text{NH}_4\text{Br}$  and ammonium iodide<sup>\*</sup>  $\text{NH}_4\text{I}$**  are white salts which crystallize in the regular system, and are isomorphous with the corresponding potassium salts. They are dissociated by heat, but the degree of dissociation of the bromide diminishes from  $320^\circ$  upwards (p. 305) and the vapor of the iodide contains much  $(\text{NH}_4\text{I})_2$ , and a little  $\text{NH}_3 + \text{HI}$ .

**Ammonium Hydroxide  $\text{NH}_4\text{OH}$ .**— The nature and behavior of this substance have been fully discussed (p. 520). It may be remarked here that its very small basic activity as compared with that of potassium hydroxide is only in part due to the low degree of ionization of its molecules. A normal solution of ammonia contains much free  $\text{NH}_3$ , besides the  $\text{NH}_4\text{OH}$  produced by its union with water. Measurement shows that two-thirds of the ammonia is not actually in the form of a base and is not in directly ionizable condition at all.

There are other indications that the amount of uncombined ammonia is considerable. Thus the organic derivative tetramethylammonium hydroxide  $N(CH_3)_4OH$  is a very active base indeed, and one of the most conspicuous differences between it and ammonium hydroxide is that it cannot decompose into water and a non-ionizable substance. It is all available for ionization, while the material in ammonia-water is not. It is also noteworthy that ammonium chloride solution is practically *neutral*, and not acid, as the solution of the chloride of a very weak base would be.

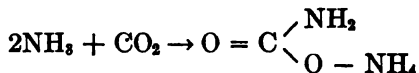
**Ammonium Nitrate  $NH_4NO_3$ .**— This is a white crystalline salt which may be made by the interaction of ammonium hydroxide and nitric acid (*cf.* p. 395). When heated gently it decomposes, giving nitrous oxide and water (p. 539). It is used as an ingredient in fireworks and explosives. It exists in no fewer than four solid physical states. The melted salt solidifies at about  $166^\circ$ , giving crystals of the regular system. When these are allowed to cool somewhat, and are held at a temperature a little below  $125.5^\circ$ , they change gradually into a mass of rhombohedral crystals, the density and all other physical properties altering at the same time. This temperature is a transition point like that at which monoclinic sulphur assumes the rhombic form (p. 412). When these rhombohedral crystals, in turn, are held at a temperature a little below  $83^\circ$  they change their form once more into crystals which belong to the rhombic system and possess a third distinct set of physical properties. Finally, below  $35^\circ$  a fourth change, into rhombic needles, takes place, and this condition of the substance is the one familiar at ordinary temperatures. All these changes proceed in the reverse order when the temperature is elevated once more.

**Ammonium Carbonate.**— When ammonium hydroxide is treated with excess of carbon dioxide the solution gives, on evaporation, **ammonium bicarbonate**  $NH_4HCO_3$ . This is a white crystalline salt which is fairly stable at the ordinary temperature. It has, however, a faint odor of ammonia, and its dissociation becomes very rapid when slight heat is applied. When a solution of this salt is treated with ammonium hydroxide, the neutral carbonate is formed:



But this salt, when left in an open vessel, loses ammonia very rapidly, and leaves the bicarbonate behind.

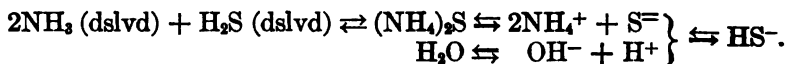
The substance commonly sold as ammonium carbonate is the so-called **sesquicarbonate**, and is made by sublimation from a mixture of ammonium chloride (or ammonium sulphate) and chalk or powdered limestone. It is a mixture, in approximately equi-molar proportions, of ammonium bicarbonate and **ammonium carbamate**. The latter is a substance related to urea, and formed when ammonia and carbon dioxide gases are mixed:



**Ammonium cyanate** is interesting on account of its rapid transformation, when warmed, into urea (p. 583). **Ammonium thiocyanate**  $\text{NH}_4\text{NCS}$  is a white salt which finds some application in analysis.

**Ammonium Sulphate.** — This is a white salt, crystallizing in rhombic prisms, which is used chiefly as a fertilizer. By electrolysis of a concentrated solution of the bisulphate, **ammonium persulphate**, which is less soluble, is formed and crystallizes out (cf. p. 449).

**Sulphides of Ammonium.** — When gaseous hydrogen sulphide and ammonia are mixed in equi-molar proportions and compressed or strongly cooled, **ammonium-hydrogen sulphide**  $\text{NH}_4\text{HS}$  is formed as a crystalline deposit on the vessel. In an open vessel, at the ordinary temperature, this solid dissociates slowly into its constituents. The **sulphide**,  $(\text{NH}_4)_2\text{S}$ , can be produced under similar conditions by using twice as much ammonia. But it is much less stable and gives up half its ammonia, producing the acid sulphide very quickly. Solutions of these sulphides, made by passing hydrogen sulphide gas into ammonium hydroxide, are much used in analysis. The sulphide is almost completely hydrolyzed by water into the acid sulphide and ammonium hydroxide, its behavior being like that of sodium sulphide (p. 418):



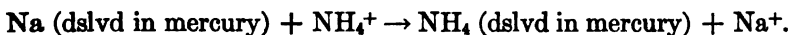
It is used for the precipitation of sulphides, such as zinc sulphide, which are insoluble in water. Although the  $\text{S}^{=2-}$  ions are not numerous at any moment, disturbance of the equilibrium by their removal, when they pass into combination, causes displacements which result in the generation of a continuous supply. The liquid smells strongly of ammonia and hydrogen sulphide on account of the dissociation of the parent molecules. Because of this dissociation, the salt is preferred

to potassium or sodium sulphide in analysis. The excess of the reagent can be driven out by simply boiling the mixture for a few minutes, all of the above equilibria being reversed. Another application in analysis depends on the tendency of this salt to unite with certain insoluble sulphides, particularly those of tin, arsenic, and antimony (*q.v.*), giving soluble complex salts.

The solution dissolves free sulphur, giving yellow **polysulphides** similar to those of potassium (p. 674). The same yellow substances are also obtained by gradual oxidation of ammonium sulphide when the solution of this salt is allowed to stand in a bottle from which the air is imperfectly excluded.

**Microcosmic Salt.** — This salt would be named, systematically, the tetrahydrate of secondary sodium-ammonium orthophosphate  $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ . When ammonium chloride and ordinary sodium phosphate are mixed in strong solution the hydrate crystallizes out. The substance is used in bead tests (*cf.* pp. 559, 560).

**Ammonium Amalgam.** — When a salt of ammonium is decomposed by electrolysis the  $\text{NH}_4$  ion, upon its discharge, gives ammonia and hydrogen, and no substance  $\text{NH}_4$  is obtained. If, however, a pool of mercury is used as the negative electrode, the  $\text{NH}_4$  forms an amalgam with it, and there seems to be no doubt that this substance is actually present in solution in the mercury. While the amalgam is being formed it swells up and gives off the decomposition products above mentioned, so that the existence of the substance is only temporary. The same material may be obtained by putting sodium amalgam into a strong solution of a salt of ammonium. The action is a displacement of one ion by another (p. 403):



This behavior is interesting since it is in harmony with the idea that ammonium, if it could be isolated, would have the properties of a metal. Substances, other than metals, are not miscible with mercury.

**Ammonium-ion  $\text{NH}_4^+$ : Analytical Reactions.** — Ionic ammonium is a colorless substance. It unites with negative ions, giving salts, which, in the majority of cases, are soluble. Ammonium chloroplatinate  $(\text{NH}_4)_2\text{PtCl}_6$ , and to a less extent ammonium hydrogen tartrate  $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$ , are insoluble compounds, and their precipitation is used as a test. The surest means of recognizing ammonium



compounds, however, consists in adding a soluble base to the substance (*cf.* p. 521). The ammonium hydroxide, which is thus formed, gives off ammonia, and the latter may be detected by its odor. The quantity of the ammonium salt present may be determined by distilling the mixture and catching the distillate in a measured volume of normal hydrochloric acid. Determination of the amount of the acid remaining unneutralized, by titration with a standard alkali solution, then gives, by difference, the quantity of ammonium hydroxide.

**Exercises.** — 1. What kind of metals will, in general, interact with solutions of bases (*cf.* p. 646)?

2. Why should a mixture of potassium chlorate and antimony trisulphide be explosive?

3. How does the direct vision spectroscope differ from the arrangement here described (*cf.* any work on physics)?

4. Why is not ammonium carbamate (p. 680) formed by the neutralization method?

5. How should you set about making, (a) a borate of potassium, (b) potassium pyrophosphate, (c) ammonium nitrite, (d) ammonium chlorate, (e) ammonium iodide?

6. Why is the cleaning of platinum wires, as usually effected by holding them in the Bunsen flame, assisted by periodical dipping into hydrochloric acid (p. 677)?

## CHAPTER XXXIV

### SODIUM AND LITHIUM. IONIC EQUILIBRIUM CONSIDERED QUANTITATIVELY

SODIUM chloride forms more than two-thirds of the solid matter dissolved in sea-water, and the great salt deposits are largely composed of it. Sea-plants contain sodium salts of organic acids, just as land-plants contain potassium salts. Chile saltpeter, cryolite, and albite (a soda felspar) are important minerals.

Compounds of sodium are usually cheaper than the corresponding ones of potassium. Also, since the atomic weight of sodium is 23, against 39 for potassium, a smaller weight of the sodium compound will produce the same chemical result. For these two reasons, sodium compounds, except in special cases, are always used for commercial purposes.

**Preparation.** — Sodium was first made by Davy (1807) by electrolysis of moist sodium hydroxide. It is manufactured by the electrolysis of fused sodium hydroxide by a method invented by Castner. The negative electrode projects through the bottom of the iron vessel containing the fused hydroxide (Fig. 142), and here the sodium and hydrogen are liberated. This electrode is surrounded by a wire-gauze partition to permit circulation in the fused mass, but prevent escape of the globules of sodium. This is surmounted by a bell-shaped vessel of iron. The positive electrode is an iron cylinder surrounding the gauze. The sodium and hydrogen liberated at the cathode, being lighter than the fused mass, ascend into the iron vessel, under the edge of which the hydrogen escapes. Oxygen is set free at the anode. The top is closed, to prevent the sodium from burning. The melted sodium is ladled into molds, like candle molds.

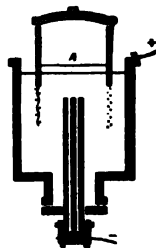


FIG. 142.

**Properties.** — Sodium is a soft, shining metal, melting at  $97.5^{\circ}$  and boiling at  $742^{\circ}$ . The green vapor is a monatomic gas. The

metal is soluble in liquefied ammonia, giving a blue solution. The **amalgam** with mercury, when it contains more than a small amount of sodium, is solid, and contains one or more compounds of the two elements. This amalgam is often used instead of the metal sodium, since the dilution or combination with mercury makes the interactions of the metal more easily controllable. Sodium is used in the manufacture of sodium peroxide, and of many complex carbon compounds which are employed as drugs and dyes.

**Sodium Hydride  $\text{NaH}$ .** — When hydrogen is led over sodium at  $364^\circ$ , in such a way that the upper part of the tube is cooler, a matted mass of fine white crystals of the hydride is deposited on the cool part of the tube. The temperature must not rise beyond  $430^\circ$ , since the compound dissociates rapidly at this temperature. The properties of the substance are similar to those of potassium hydride (p. 663).

**Sodium Chloride  $\text{NaCl}$ .** — Common salt is obtained from the salt deposits of Stassfurt, Reichenhall (near Salzburg), in Cheshire, at Syracuse and Warsaw in New York, at Salina in Kansas, in Utah, California, and many other districts. Natural brines are obtained from wells in various parts of the world. Since the salt can seldom be used directly, on account of impurities which it contains, it is purified by recrystallization from water. Natural brines, which are sometimes dilute, are often concentrated by dripping over extensive racks composed of twigs. When the resulting brine is allowed to evaporate slowly by the help of the sun's heat, large crystals, sold as "solar salt," are obtained. By the use of artificial heat and stirring, smaller crystals of greater purity can be secured. In northern Russia, the brine is allowed to freeze, and the water thus removed in the form of ice (p. 199). Salt intended for table use must be freed from the traces of magnesium chloride (*q.v.*) present in the original brine or deposit, for this impurity causes it to absorb moisture more vigorously from the air. Addition of a little baking soda  $\text{NaHCO}_3$  remedies the difficulty, by forming the insoluble magnesium carbonate. The purest salt for chemical purposes is precipitated from a saturated solution of salt by leading into it hydrogen chloride gas. Explanation of this effect will be given presently (see p. 699).

Common salt crystallizes in cubes, the faces of which are usually hollow. The crystals decrepitate (p. 670) when heated, and melt at about  $820^\circ$ . Common salt is the source of all sodium compounds,

with the exception of the nitrate. From it come also most of the chlorine and hydrogen chloride used in commerce.

**The Hydroxide and Oxides.**—Sodium hydroxide  $\text{NaOH}$  is prepared both by the action of slaked lime upon sodium carbonate and by the electrolysis of a solution of sodium chloride, precisely as is potassium hydroxide (p. 666).

Sodium hydroxide is a highly deliquescent substance, which, when exposed to the air, first liquefies and then becomes solid on account of the formation of sodium carbonate. Its general chemical properties are identical with those of potassium hydroxide. It is used in the manufacture of soap, in the preparation of paper pulp, and in many other chemical industries.

**Sodium peroxide**  $\text{Na}_2\text{O}_2$  is made by heating sodium at  $300\text{--}400^\circ$  in air which has been freed from carbon dioxide. The sodium is placed on trays of aluminium, and is passed into the furnace against the current of air. In this way, the freshest sodium meets the air from which most of the oxygen has been removed, and the action is moderated. Conversely, the almost entirely oxidized sodium meets the freshest air, and completion of the oxidation is thus assured. This oxide is the sodium salt of hydrogen peroxide. When thrown into water, it decomposes in part, in consequence of the heat developed, giving sodium hydroxide and oxygen. With careful cooling, however, much of it can be dissolved. By interaction with acids it yields hydrogen peroxide. Sodium peroxide is now used commercially for oxidizing and bleaching and, in the form of oxone (p. 85), as a source of oxygen. The ordinary **sodium oxide**  $\text{Na}_2\text{O}$  is made in the same way as is potassium oxide (p. 668).

**The Nitrate and Nitrite.**—The occurrence and purification of **sodium nitrate**  $\text{NaNO}_3$  have already been described (p. 525). Its crystals are of rhombohedral form (Fig. 69, p. 173). This salt is one of the best of fertilizers, since it furnishes to plants the nitrogen which they require in very soluble form. It is used also in the manufacture of potassium nitrate, of nitric acid, and of sodium nitrite.

**Sodium nitrite**  $\text{NaNO}_2$  is formed by heating sodium nitrate with metallic lead and recrystallizing the product (p. 538). Although very soluble it is less so than potassium nitrite, and is therefore more easily prepared in pure condition. It is used as a source of nitrous acid by manufacturers of organic dyes.

**Manufacture of Sodium Carbonate.**— Natural sodium carbonate is found in Egypt and in other parts of the world. At Owen's Lake, California, it is secured by solar evaporation of the water. The sesquicarbonate  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ , being the least soluble of the carbonates of sodium, is the one deposited. Locally, small quantities of sodium carbonate are still made by the burning of sea-weed. Up to the close of the eighteenth century this was the only source of the compound, and the product from Spain, known commercially as *barilla*, was ten times as expensive as the carbonate now is. Hence glass and soap were proportionately dearer than at present.

In 1791 the French Academy offered a prize for the discovery of an inexpensive method for the preparation of sodium carbonate from common salt, and **Le Blanc** proposed the process which bears his name

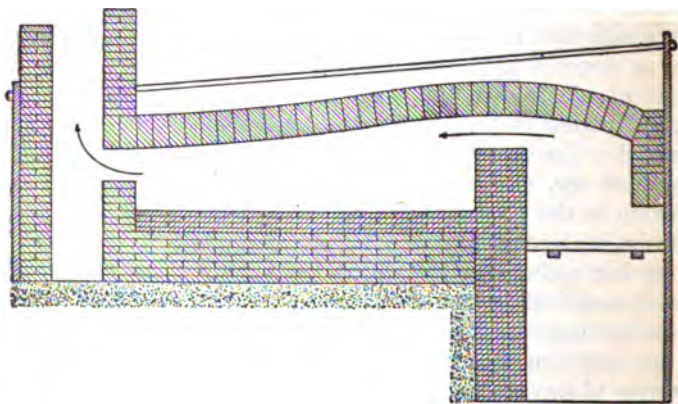
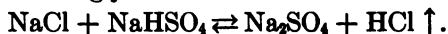


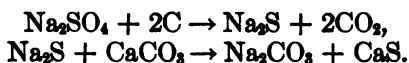
FIG. 143.

and is still in use in two factories in Europe. During the Revolution his factory was destroyed, his patents were declared to be public property, and the inventor died by suicide. The chief stages of Le Blanc's process involve three chemical actions. In the first place, sodium chloride is treated with an equivalent amount of sulphuric acid in a large cast-iron or earthenware pan. The bisulphate thus produced (*cf.* p. 206), together with the unchanged sodium chloride, is raked out on to the hearth of a reverberatory\* furnace (Fig. 143) and heated more strongly:



\* So called because the heated gases from the fire are *deflected* by the roof and play upon the materials spread on the bed of the furnace. -

The product of this treatment is called *salt-cake*. The second and third actions which follow are conducted in one operation. They consist in the reduction of the sodium sulphate by means of powdered coal and the interaction of the resulting sulphide of sodium with chalk or powdered limestone:



Formerly, the salt-cake, limestone, and coal were stirred upon the hearth of a reverberatory furnace and worked by hand. The material was collected into balls, and the end of the action was recognized by the fact that bubbles of carbon monoxide began to force their way to the surface and caused little jets of blue flame. The gas is produced by the action of the coal upon the calcium carbonate, excess of both of these substances being present:  $\text{CaCO}_3 + \text{C} \rightarrow \text{CaO} + 2\text{CO}$ . The production of this gas gives a porous texture to the material, which facilitates the solution of the sodium carbonate in the final stage. The porous product is called *black-ash*. In modern factories hand labor is saved by giving the black-ash furnace the form of a rotating cylinder, in which projections from the walls assist in bringing about complete mixing of the materials during the action.

The black-ash varies very much in composition. It commonly contains 45 per cent of sodium carbonate, 30 per cent of calcium sulphide, 10 per cent of calcium oxide, and a number of other products and impurities. The coal used in the operation is selected so as to be as free as possible from combined nitrogen, the presence of which leads to the formation of cyanides.

Calcium sulphide is not very soluble in water, and is but slowly hydrolyzed by it (p. 421), especially when calcium hydroxide is present. The sodium carbonate is therefore extracted from the black-ash by water. The ash is placed in a series of vessels at different levels, and a stream of water flows from one vessel to another, until, when it issues from the last, it is completely saturated with sodium carbonate. A temperature of 30° to 40°, at which the solubility of sodium carbonate is at a maximum, is employed. When the material in the first of the vessels has been exhausted, the water is allowed to enter the second vessel directly, and a vessel containing fresh black-ash is added at the lower end of the series. In this way the most nearly exhausted ash comes in contact with pure water, which is in the best position to dissolve the remaining sodium carbonate rapidly,

while the fresh black-ash encounters a solution already almost at the point of saturation.

The saturated solution is evaporated in shallow pans placed in the flues of the furnaces, and the monohydrate  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , which crystallizes from the hot liquid, is raked out and dried by heat, leaving **calcined soda**. When this material is recrystallized from water and is allowed to deposit itself from the solution at the ordinary temperature, the decahydrate  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , **soda crystals**, **washing soda**, or **sal soda** appears.

The **Solvay**, or **ammonia-soda process**, invented in 1860, has now displaced the Le Blanc process. It differs from the latter by involving almost nothing but ionic actions. A solution of salt containing ammonia and warmed to  $40^\circ$  fills a tower divided by a number of perforated partitions. Carbon dioxide, which is forced in below, makes its way up through the liquid. The ammonium bicarbonate formed by its action undergoes double decomposition with the salt, and sodium bicarbonate which is precipitated settles upon the partitions:



The solid sodium bicarbonate, after being freed from the liquid, is heated strongly and leaves behind sodium carbonate:



The carbon dioxide which is liberated passes through the operation once more. The supply of carbon dioxide is generated in lime-kilns of special form. The mother-liquor from the sodium bicarbonate contains ammonium chloride. This is decomposed by heating with quicklime from the kilns, and the ammonia which is thus obtained is available for the treatment of another batch. A solution of calcium chloride is thus the only waste product. Some of this is used for laying dust on roads, because, being a deliquescent salt, the moistened dust does not dry up.

This process furnishes a much purer product than does the Le Blanc process. A possible rival threatens to arise in the treatment of electrolytic sodium hydroxide with carbon dioxide gas.

**Properties of Sodium Carbonate.**—The common form of sodium carbonate consists of large monoclinic crystals of the decahydrate  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . This substance has a fairly high aqueous ten-

sion, and loses nine of the ten molecules of water which it contains when it is exposed in an open vessel. When warmed it melts at  $35.2^{\circ}$ , giving a solution of sodium carbonate in water. The residue from evaporation, above  $35.2^{\circ}$ , is the **monohydrate**  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ . At higher temperatures, or with low atmospheric aqueous tension (p. 152), this in turn can be completely dehydrated. The decahydrate increases in solubility up to  $35.2^{\circ}$ , when it ceases to exist. Just above this temperature the monohydrate is the only substance which is stable. The solubility of the monohydrate is the same as that of the decahydrate at  $35.2^{\circ}$ , and diminishes as the temperature is raised. The relations are of the same nature as in the case of sodium sulphate (p. 193). In aqueous solution, sodium carbonate is hydrolyzed (3.2 per cent in 0.1N sol. at  $25^{\circ}$ ), and shows a marked alkaline reaction. The compound is used in large amounts for the manufacture of glass and soap, in the softening of water, and is applied in innumerable ways in the scientific industries for purposes akin to cleansing.

All the familiar salts of sodium, excepting sodium nitrate and the peroxide, are made by the treatment of sodium carbonate or sodium hydroxide with acids.

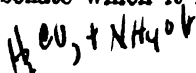
**Sodium Bicarbonate  $\text{NaHCO}_3$  or Baking Soda.**— This salt is formed in the Solvay process, and can be prepared in a state of purity by passing carbon dioxide over the decahydrate of sodium carbonate:



The hydrate is spread upon a grating, through which the water generated by the action drips away. This action is reversible, and sodium bicarbonate shows, even in the cold, an appreciable tension of carbon dioxide. Even a solution of this salt gives off carbon dioxide, when boiled. An aqueous solution of *pure* sodium bicarbonate is neutral to phenolphthalein, on account of the small degree of ionization of the ion  $\text{HCO}_3^-$ . Ordinarily, however, the solution is alkaline, on account of the presence of the carbonate, which is hydrolyzed.

**Baking Powders.**— The object of using the powder is to generate carbon dioxide in the dough. The bubbles are retained because of the presence of the sticky gluten. They expand when the dough is heated in baking, and give to the bread its porous texture.

Baking soda, alone, will give off carbon dioxide, but the sodium carbonate which it leaves behind has a disagreeable taste and acts





upon the gluten causing a yellow color and unpleasant smell. It also tends to neutralize the acid in the gastric juice and so impedes digestion. To prevent this result, sour milk (containing lactic acid) and even vinegar are added. Usually, however, a **baking powder** containing an acid substance along with the bicarbonate is employed. Potassium bitartrate (**cream of tartar**)  $\text{KHC}_4\text{H}_4\text{O}_6$  (p. 608) is most commonly employed, although alum and primary sodium orthophosphate (p. 558) are also used:



The cream of tartar has the advantages that it is somewhat insoluble and does not act noticeably upon the soda before the mixing of the dough is complete, and that the sodium-potassium tartrate (**Rochelle Salt**) produced is not harmful. A little starch is added to baking powders to keep the particles of the two other ingredients apart, and prevent gradual interaction before use.

For raising bakers' bread, yeast is employed, and time is allowed for the propagation of the yeast and its action upon the sugar (p. 607) in the flour. A little molasses or malt extract is often added, to ensure a sufficient supply of sugar.

The whites of eggs cause cake to rise, largely because they are whipped before use, and bubbles of air, which expand when heated, are thus introduced.

**Sodium Sulphate**  $\text{Na}_2\text{SO}_4$ .—Anhydrous sodium sulphate (thenardite) crystallizes in the rhombic system, and is found in the salt layers. The same salt is contained in mineral waters, such as those of Friedrichshall and Karlsbad. It is formed in connection with the manufacture of nitric acid from sodium nitrate. Some of it is also prepared at Stassfurt by dissolving kieserite  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  in water along with sodium chloride. When the solution is cooled to  $0^\circ$ , the decahydrate of sodium sulphate crystallizes out, and magnesium chloride remains in solution. It is used, as a substitute for sodium carbonate, in making inexpensive glass.

The **decahydrate of sodium sulphate**  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , **Glauber's salt**, forms large monoclinic crystals which give up all the water of hydration when kept in an open vessel. When heated the crystals melt at  $32.4^\circ$ , and are resolved into the sulphate and water. The relations of the hydrate and anhydrous substance in respect to solubility have been fully discussed already (p. 193). When the decahydrate is mixed with concentrated hydrochloric acid, it is decomposed, and a

part of the sulphate is converted into sodium chloride, the second action being a reversible one. This is one of those actions which proceed spontaneously, and therefore involve a diminution in the store of available energy in the system, although, so far as *heat* is concerned, a marked absorption of this form of energy takes place (*cf.* p. 35). The combination is used, in fact, as a freezing mixture.

**Sodium Thiosulphate  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ .** — This salt is made by boiling a solution of sodium sulphite with sulphur. It is also obtained by boiling sulphur with caustic soda, and crystallizes from the mixed solution:



It gives large, transparent monoclinic crystals of a pentahydrate. When heated it first loses the water of hydration, and then decomposes, giving sodium sulphate, which is the most stable oxygen-sulphur compound of sodium, and sodium pentasulphide:



From the latter, four unit-weights of sulphur can be driven by stronger heating. Sodium thiosulphate (*hypo*) is used for fixing negatives in photography (*q.v.*), and by bleachers as antichlor (p. 448). For sodium hyposulphite  $\text{Na}_2\text{S}_2\text{O}_4$ , see p. 443.

**Phosphates of Sodium.** — Common sodium phosphate is a dodecahydrate of the secondary orthophosphate,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . It is made by neutralization of phosphoric acid with sodium carbonate, and crystallizes from the solution in large, transparent monoclinic prisms. Its properties have already been discussed (p. 559).

Sodium metaphosphate  $\text{NaPO}_3$  is used for bead tests (*cf.* p. 560).

**Sodium Tetraborate  $\text{Na}_2\text{B}_4\text{O}_7$ , or Borax.** — This salt combines with ten molecules of water, forming large, transparent prisms,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . When heated it loses water, and leaves the easily fusible anhydrous salt in glassy form. Its sources have already been discussed under borates (p. 637). It is used as an ingredient in glazes for porcelain, in soldering, for bead reactions (*cf.* p. 640), and for preserving foods.

**Sodium Disilicate  $\text{Na}_2\text{Si}_2\text{O}_5$ .** — This salt (p. 634) is used for fireproofing wood and other materials and for preserving eggs. Sand

which is moistened with it and pressed in molds, forms, after baking, a serviceable artificial stone. Since silicic acid is a feeble acid, this salt is hydrolyzed, and gives a strongly alkaline solution (p. 648). For **sodium cyanide**, see p. 721.

**Properties of Sodium-ion  $\text{Na}^+$ : Analytical Reactions.**—Sodium-ion is a colorless ionic material which unites with all negative ions. Practically all the salts so formed are soluble in water. The only ones which can be precipitated are sodium fluosilicate  $\text{Na}_2\text{SiF}_6$ , made by the addition of hydrofluosilicic acid to a strong solution of a sodium salt, and sodium-hydrogen pyroantimoniate  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ , made by similar addition of the corresponding potassium salt. The two yellow lines in the spectrum are characteristic. If the yellow light persists longer than could be accounted for by the ordinary deposit of dust on the wire, a sodium compound is present in the material.

### LITHIUM

The compounds of lithium are made from amblygonite, a mixed phosphate and fluoride of aluminium and lithium. It occurs in lepidolite (a lithia mica) and in other rare minerals. Traces of compounds of the element are found widely diffused in the soil, and are taken up by plants, particularly tobacco and beets, in the ashes of which the element may be detected spectroscopically.

The **metal** is liberated by electrolysis of the fused chloride, the manipulation being facilitated by the addition of some potassium chloride to lower the melting-point of the lithium salt. The melting-point and boiling-point of the free element are higher than those of any other alkali-metal, and the specific gravity (0.53) is lower than that of any other metal whatever. Lithium not only floats upon water, but also in the petroleum in which it is preserved.

The metal behaves towards water and oxygen like sodium (p. 115). It unites directly and vigorously with hydrogen ( $\text{LiH}$ ), nitrogen ( $\text{Li}_3\text{N}$ ), and oxygen ( $\text{Li}_2\text{O}$ ), forming stable compounds. The chloride crystallizes in octahedra (p. 172). The relative insolubility (Table) of the hydroxide  $\text{LiOH}$ , the carbonate  $\text{Li}_2\text{CO}_3$ , and the phosphate  $\text{Li}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , is in sharp contrast to the easy solubility of the corresponding compounds of the other alkali-metals, and links lithium with magnesium. The compounds of lithium give a bright-red color to the Bunsen flame, and a bright-red and a somewhat less bright orange line are seen in the spectrum. The carbonate is used in medicine.

## IONIC EQUILIBRIUM, CONSIDERED QUANTITATIVELY

**The Simple Case.**—In view of the predominance of ionic actions in the chemistry of the metals, and of the determinative effect of ionic equilibria on many actions, it is essential that we should be prepared in future for a more exact study of these phenomena than we have hitherto attempted. The whole *basis* for this exact study *has already been supplied*, and only more specific application of the principles is demanded. The basis referred to, which should now be re-read as a preliminary to what follows, is contained in, (1) the discussion of chemical equilibrium in general (pp. 287–295), (2) the application of the same principles to ionic equilibrium (p. 359), and (3) the illustration of this application in the case of cupric bromide (pp. 378–380).

In the first place, the principles themselves must be recalled. When acetic acid, for example, is dissolved in water, it is ionized thus:



The amount of molecular acetic acid dissociated per second in a given amount of the solution is proportional to the concentration of the molecules, while the amount of the two ionic materials, hydrogen-ion and acetate-ion, uniting to form molecules of acetic acid depends on the frequency of the encounters of the two kinds of ions and is proportional to the ionic concentrations (p. 358). The unit of concentration (p. 294) is 1 mole per liter, or, in the present case, 60 g. of the acid, 1 g. of hydrogen-ion, and 59 g. of acetate-ion, respectively, per liter, for these numbers represent the weight of one mole of each component. According to the law of concentration (p. 297):

$$\frac{[\text{H}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = K, \quad (1)$$

and the numerical value of this fraction, or of  $K$ , remains unchanged whatever the total concentration of the solution may be. If the solution is diluted, for example,  $[\text{H}^+]$  and  $[\text{C}_2\text{H}_3\text{O}_2^-]$  diminish relatively less quickly than  $[\text{HC}_2\text{H}_3\text{O}_2]$  in order that the value of the whole expression may remain the same. This is accomplished by ionization of a part of the material whose concentration is  $[\text{HC}_2\text{H}_3\text{O}_2]$  and its transference to the ionic forms whose concentrations are  $[\text{H}^+]$  and  $[\text{C}_2\text{H}_3\text{O}_2^-]$ , respectively (p. 299).

A numerical example will show that this law of concentration expresses the facts with considerable exactness. The data in regard to acetic acid are as follows (p. 365):

Acetic Acid.	I. Molar Con- centration.	II. Proportion of Whole Mate- rial Ionised.	III. [H <sup>+</sup> ] and [C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup> ] (I × II).	IV. [HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ] (I - III).
Uni-molar . . .	1.0	0.004	0.004	1.0 - 0.004
Deci-molar . . .	0.1	0.013	0.0013	0.1 - 0.0013
Centi-molar . . .	0.01	0.0407	0.000407	0.01 - 0.000407

Now  $[H^+] = [C_2H_3O_2^-]$ , since the ions are produced in equal numbers. Also, for our purpose, the numbers to be subtracted in column iv are relatively so small that the values 1, 0.1, and 0.01 may be taken to represent  $[HC_2H_3O_2]$  without appreciable error. Hence, substituting the data in equation (1) above, we have:

$$\frac{(.004)^2}{1} = .0160. \quad \frac{(.0013)^2}{.1} = .0169. \quad \frac{(.000407)^2}{.01} = .0165.$$

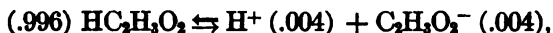
In other words, although the last solution is a hundred times more dilute than the first, and the degree of ionization has increased ten times, the whole expression remains close to the value 0.0165 and is essentially constant.

When conductivity data, like the above, are applied in the same way to the cases of more highly ionized substances, the values of  $K$  are less nearly constant. It is supposed that with this class of substances the measurements of degrees of ionization by the conductivity method are less accurate, although the cause of the discrepancy has not been fully determined. However, in the very general applications of the data, which are all that we shall be required to make, the conclusions will not be affected by this fact.

**Excess of One Ion.** — In the case of cupric bromide (p. 378), we showed that increasing the concentration of the bromide-ion displaced the equilibrium by favoring the union of the ions to form molecular cupric bromide:  $2Br^- + Cu^{++} \rightarrow CuBr_2$ . This we speak of as a **repression of the ionization** of the cupric bromide. Now, if the substance is a *slightly* ionized one, like a weak acid or a weak base, the repression of the ionization through the formation of molecules in this way may remove so many of that one of the ions which is not present in excess (corresponding to the  $Cu^{++}$  in the foregoing illustration), that the mixture will no longer respond to tests for the ion so removed. This is an interesting and very common case. The

behavior of acetic acid, a weak, slightly ionized acid, will serve as an illustration.

In normal solution (60 g. in 1 l.) acetic acid is only .004 ionized (p. 694), so that, in the equation for the equilibrium,



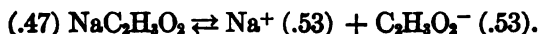
the relative proportions are as shown by the numbers in parenthesis. If the whole of the acid (60 g.) were ionized, there would be 1 g. of hydrogen-ion per liter. Yet, even in this much smaller concentration (.004 g. per liter), the acid taste of the  $\text{H}^+$  and its effect upon indicators can be distinctly recognized. If, *now*, solid sodium acetate is dissolved in the solution, the liquid *no longer gives an acid reaction* with one of the less delicate indicators, like methyl orange (*q.v.*). The explanation is simple. Sodium acetate is highly ionized. It gives, therefore, a large concentration of acetate-ion to a liquid formerly containing very little. This causes a greatly increased union of the  $\text{H}^+$  ions and  $\text{C}_2\text{H}_3\text{O}_2^-$  ions, and the former, being already very few in number, disappear almost entirely. Hence the solution becomes, to all intents and purposes, neutral. There is no less *acetic acid* present than before, but the concentration of hydrogen-ion is very much smaller.

**Formulation and Quantitative Treatment of the Case of Excess of One Ion.**—If the semi-mathematical mode of formulating an equilibrium (p. 359), as applied to the case of an ionogen, be employed here, the foregoing general statements may be made more precise and the conclusions clearer. The value of  $K$  is constant, whether the strength of the solution of acetic acid is great or small, *and even when another substance with a common ion is present*. In the latter case,  $[\text{C}_2\text{H}_3\text{O}_2^-]$  and  $[\text{H}^+]$  stand for the *whole* concentrations of each of these ionic substances from *both* sources.

Now, as we have seen, in normal acetic acid  $[\text{H}^+] = .004$ ,  $[\text{C}_2\text{H}_3\text{O}_2^-] = .004$  (for the number of each kind of ions is the same), and  $[\text{HC}_2\text{H}_3\text{O}_2] = .996$ , practically 1. Substituting in the formula

$$\frac{0.004 \times 0.004}{1} = K (= 0.0416).$$

When sodium acetate is dissolved in the liquid until the solution is normal in respect to this substance *also*, the following additional equilibrium has to be considered:



The concentration of acetate-ion from this source is .53, so that, in the mixture of acid and salt, the concentration of acetate-ion  $[C_2H_3O_2^-]$  will be  $.53 + .004 = .534$ , or nearly 134 times larger than in the acid alone. Hence, in order that the product  $[H^+] \times [C_2H_3O_2^-]$  may recover, as it must, a value much nearer to the old one,  $[H^+]$  must be diminished to something like  $\frac{1}{134}$  of its former magnitude. That is,  $[H^+]$  will become equal to about 0.00003,  $\frac{0.00003 \times 0.534}{1} =$

$K (=0.0416)$ , the rest of the hydrogen-ion uniting with a corresponding amount of the acetate-ion to form molecular acetic acid. The effect of adding this amount of sodium acetate therefore is, as we have seen, to reduce the concentration of the hydrogen-ion below the amount which can be detected by use of an indicator like methyl orange.

This effect is of course reciprocal, and the ionization of the sodium acetate will be reduced also. But the acetate-ion furnished by the acetic acid is relatively so small in amount (.00003 against .53) that the effect it produces on the ionization of the salt is imperceptible.

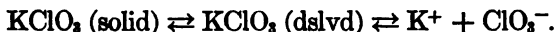
It will be noted that the acetate-ion and hydrogen-ion disappear in equivalent quantities, for they unite. There is, however, so much of the former that the loss it suffers goes unremarked, while there is so little of the latter that almost none of it remains. When substances of more nearly equal degrees of ionization are used, *both effects are equally inconspicuous*. Thus, sodium chloride and hydrogen chloride in normal solutions yield approximately equal concentrations of chloride-ion (.784 and .676). Hence, if one mole of sodium chloride were to be dissolved in the portion of water already containing one mole of hydrogen chloride, the concentration of the chloride-ion, at a very rough estimate, would be nearly doubled. If this doubling of the concentration of chloridion almost halved that of the hydrogen-ion (.784), in order that the expression  $[Cl^-] \times [H^+] \div [HCl]$  might remain constant, the concentration of the hydrogen-ion would still be about .400 and therefore 100 times as great as in molar acetic acid. It is thus altogether impossible to reduce the concentration of the hydrogen-ion given by an *active* acid like hydrochloric acid below the limit at which indicators are affected, for there is no way of introducing the enormous concentration of the other ion which the theory demands.

With more crude means of observation than indicators afford, effects like this last may sometimes be rendered visible. This was the case with cupric bromide solution, to which potassium bromide

was added (p. 379). The blue of the cupric-ion disappeared from view, while much cupric-ion was still present, because the brown color of the molecular cupric bromide covered it up completely.

**Special Case of Saturated Solutions.**—The commonest as well as the most interesting application of the conceptions developed above is met with in connection with saturated solutions, especially those of relatively insoluble substances.

The situation in a system consisting of the saturated solution and excess of the solute has been discussed already (read p. 382). In the case of potassium chlorate, for example, we have the following scheme of equilibria:



Solution of the solid is promoted by the solution pressure of the molecules, while it is opposed by the diffusion pressure of the dissolved substance, and the solution is saturated when these tendencies produce equal effects (p. 186). Now it must be noted that the tendency *directly* opposed to the solution pressure is the *partial* diffusion pressure of the dissolved *molecules* alone. The chief contents of the solution, the molecules and two kinds of ions of the salt, and any foreign material that may be present, are like a mixture of gases, and the principle of partial pressure (p. 111) is to be applied. The ions and the foreign material do not deposit themselves upon the solid, and take, therefore, no part *directly* in the equilibrium which controls solubility. In respect to this the ions are themselves foreign substances. Hence the conclusion may be stated that, in solutions saturated at a given temperature by a given solute, the concentration of the dissolved molecules of the solute considered by themselves will be constant whatever other substances may be present.

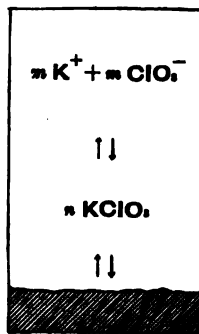


FIG. 144.

The total "solubility" of a substance, as we have used the term hitherto, is made up of a molecular and an ionic part. The latter, as we shall presently see, is not constant when a foreign substance containing a common ion is already in the liquid. Since the treatment of the subject requires us now to distinguish between the two portions of the solute, a diagram (Fig. 144) will assist in emphasizing the distinction. The material at the bottom is the salt. The molecules and ions are to be thought



of as being mixed and as being present in numbers represented by the factors  $n$  and  $m$ . Since no foreign body is present, the two ions in this case are equal in number.

When we now apply these ideas to the mathematical expression of the relation:

$$\frac{[K^+] \times [ClO_3^-]}{[KClO_3]}$$

we perceive that, in a *saturated* solution,  $[KClO_3]$ , the concentration of the molecules, is *constant*. Transposing, we have

$$[K^+] \times [ClO_3^-] = K [KClO_3] = K'.$$

Hence the relation leads to the important conclusion that, in a *saturated* solution the product of the molar concentrations of the ions is constant.\* This product is called the *ion-product constant* for the substance. The *law of the constancy of the ion-product in a saturated solution* is one of the most useful of the principles of chemistry. It enables us to explain all the varied phenomena of precipitation and of the solution of precipitates in a consistent manner. These applications of the principle will be explained in the next chapter. One curious kind of precipitation will be described here, however, as an illustration of the use of the principle.

#### *Illustration of the Principle of Ion-Product Constancy.*—

When, to a *saturated* solution of one of the less soluble salts, a strong solution of a salt having *one ion in common* with the first salt is added, precipitation of the first salt frequently takes place. This happens, for example, with a saturated solution of potassium chlorate, which is not very soluble (molar solubility 0.52, see Table). The concentrations  $[K^+]$  and  $[ClO_3^-]$  being small, one may easily increase the value for one of the ions, say  $[ClO_3^-]$ , fivefold, by adding a chlorate which is sufficiently soluble. To preserve the value of the product  $[K^+] \times [ClO_3^-]$ , the value of  $[K^+]$  will then have to be diminished at once to one-fifth of its former value. This can occur only by union of the ionic material it represents with an equivalent amount of that for

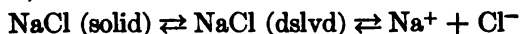
\* The principle of constant concentration of dissolved molecules, stated above, has been shown to express the facts very inaccurately. Now the principle of the constancy of the ratio of the ion-product to the concentration of the molecules is also inaccurate in the case of highly ionized substances, yet in such a way that the two errors neutralize one another. Thus, the principle of ion-product constancy here given is in itself fairly exact.

which  $[\text{ClO}_3^-]$  stands. The molecular material so produced will thus tend at first to swell the value of  $[\text{KClO}_3]$ . But the value of  $[\text{KClO}_3]$  cannot be increased, for the solution is *already saturated with molecules*, so that the **new supply of molecules**, or others in equal numbers, **will be precipitated**. Hence the ionic part of the dissolved substance may be diminished, the equilibria (p. 697) may be partially reversed, and we may actually precipitate a part of the dissolved material without introducing any substance, which, in the ordinary sense, can interact with it.

In point of fact, when, to a saturated solution of potassium chlorate there is added a saturated solution of potassium chloride  $\text{KCl}$  or of sodium chlorate  $\text{NaClO}_3$ , a precipitate of potassium chlorate is thrown down. These two salts, containing each one of the ions of  $\text{KClO}_3$ , and being much more soluble than the latter (see Table), increase the concentration of one ion and cause the precipitation in the fashion just explained.

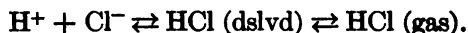
The product of the concentrations of the ions, for example  $[\text{K}^+] \times [\text{ClO}_3^-]$ , is called also the **solubility product**, because these two values jointly determine the magnitude of the solubility of the substance. The solubility of the molecules is irreducible, but the ionic part of the dissolved material may become vanishingly small if the value of either  $[\text{X}^+]$  or  $[\text{Y}^-]$  is very minute. The ionic part of any particular substance is made up of the smaller of the two concentrations of the ionic substances which it yields, plus an equivalent amount, and no more, of the concentration of the other ion. The rest of the other ionic substance is part of the solubility of some other component.

**Other Illustrations.**—The precipitation of sodium chloride from a saturated solution, by the introduction of gaseous hydrogen chloride (p. 684), is to be explained in the same way. The equilibria:



are reversed by the introduction of additional  $\text{Cl}^-$  from the very soluble, and highly ionized  $\text{HCl}$ .

A steady stream of hydrogen chloride is often obtained by dropping concentrated sulphuric acid into saturated hydrochloric acid:



The effect is due in part to repression of the ionization of the hydrogen chloride and elimination of molecules of the gas from the water, which is already saturated with molecules of the same kind.

The formation of potassium hydroxide (p. 666) ceases when a certain concentration has been reached. This occurs because the concentration of  $\text{OH}^-$ , which rapidly increases, is a factor in the solubility product of calcium hydroxide,  $[\text{Ca}^{++}] \times [\text{OH}^-]^2$ . With much  $\text{OH}^-$ , little  $\text{Ca}^{++}$  is required to give the constant, numerical value of the product. When the concentration  $[\text{Ca}^{++}]$  from the hydroxide has become about as small as that from the carbonate, the motive for the interaction has been removed. This principle is thus as important in industrial operations as it is in analytical and other laboratory experimentation.

**Exercises.** — 1. The vapor density of sodium peroxide has not been determined. Why is the formula  $\text{Na}_2\text{O}_2$  assigned to it?

2. Construct a scheme of equilibria (p. 687) showing the hydrolysis of calcium sulphide. Why does the presence of calcium hydroxide diminish the tendency to hydrolysis?

3. What will be the effect of adding a concentrated solution of silver nitrate to a saturated solution of silver sulphate or of silver acetate (see Table of solubilities)?

4. Although a 20 per cent solution of soap can easily be made, a 0.5 per cent solution can be salted out (p. 623). How does this fact show that salting out is *not* an operation like the precipitations just discussed?

5. One equivalent or *less* of concentrated sulphuric acid interacts in the cold with sodium carbonate to give normal sodium sulphate, and with sodium chloride to give sodium-hydrogen sulphate (p. 206). Why this difference? Which of the two products would be obtained by the action of cold concentrated sulphuric acid on, (a) sodium sulphite, (b) sodium nitrate, (c) sodium nitrite?

## CHAPTER XXXV

### METALLIC ELEMENTS OF THE ALKALINE EARTHS

#### CALCIUM, STRONTIUM, BARIUM

*The Chemical Relations of the Elements.* — The metals of this group, calcium (Ca, at. wt. 40.07), strontium (Sr, at. wt. 87.63), and barium (Ba, at. wt. 137.37), constitute a typical chemical family, both in the qualitative resemblance to one another of the elements and of the corresponding compounds, and in the quantitative variation in the properties with increasing atomic weight. The metals themselves displace hydrogen vigorously from cold water, giving hydroxides. The solutions of these hydroxides, although dilute, on account of a rather small solubility, are strongly alkaline in reaction. The high degree of ionization of the hydroxides recalls the hydroxides of the metals of the alkalies, and their relative insolubility the hydroxides of the "earths" (*q.v.*).

In all their compounds, calcium, strontium, and barium are bivalent. The hydroxides are formed by union of the oxides with water and are progressively less easy to decompose by heating, barium hydroxide being the hardest. The carbonates, when heated, yield the oxide of the metal and carbon dioxide, barium carbonate being the most difficult to decompose. The nitrates, when heated moderately, give the nitrites, but the latter are broken up by heating and yield the oxide of the metal, and nitrogen tetroxide. In these and other respects the compounds of the metals of the alkaline earths resemble those of the heavy metals and differ from those of the metals of the alkalies. Barium approaches the latter most nearly.

The table of solubilities shows that the chlorides and nitrates of calcium, strontium, and barium are all soluble in water, the solubility diminishing in the order given. The sulphates and hydroxides cover a wide range from slight solubility to extreme insolubility. Of the sulphates, 2000, 110, and 2.3 parts, respectively, dissolve in one million parts of water. In the case of the hydroxides the order of magnitudes is reversed, and the corresponding numbers are 1700, 7700, and 37,000. The carbonates are almost as insoluble as is

barium sulphate. The element radium (Ra, at. wt. 226), belongs to this family (see under Uranium).

### CALCIUM Ca

**Occurrence.** — The fluoride, and the various forms of the carbonate, sulphate, and phosphate which are found in nature, are described below. As silicate, calcium occurs, along with other metals, in many minerals and rocks. It is found also in plants, and its compounds are important constituents of the bones and shells of animals.

**The Metal.** — Although the alkali metals can be liberated by heating the carbonates with carbon, the metals of the present family are not obtainable by this means. This may be due, in part, to imperfect contact between the materials in consequence of the infusibility of the oxides. Calcium is most easily made by electrolysis of the molten chloride, to which calcium fluoride is added to lower the melting-point. A hollow cylinder, made of blocks of carbon bolted together and open above, forms the anode. A rod of copper hanging so that its end dips into the melt forms the cathode. The melting of the anhydrous calcium chloride with which the cylinder is filled is started by means of a thin rod of carbon laid across from the anode to the cathode. When the heat generated by the passage of the current through this highly resisting medium has melted a sufficient amount of the salt, the rod is removed, and the resistance of the fused material suffices to maintain the temperature. The calcium rises round the cathode and collects on the surface of the bath. By slowly elevating the copper cathode, the calcium, which adheres to it, may be drawn out of the fused mass in the form of a gradually lengthening, irregular rod. The rod of calcium is kept constantly in contact with the metal which accumulates on the surface, and thus forms one of the electrodes.

Calcium is a silver-white, crystalline metal (m.p. 750°, density 1.85) which is a little harder than lead, and can be cut, drawn, and rolled. Only four metals (p. 645) are better conductors of electricity. It interacts vigorously with water. When dry and cold it is inactive, but when heated it unites vigorously with hydrogen, oxygen, the halogens, and nitrogen. It burns in the air, giving a mixture of the oxide and nitride  $\text{Ca}_3\text{N}_2$ . The presence of the latter may be shown by the liberation of ammonia when water is brought in contact with the residue:



**Calcium Hydride  $\text{CaH}_2$ .** — The white crystalline hydride  $\text{CaH}_2$  is formed by direct union of the constituents. It is known in commerce as **hydrolyte**, and is an expensive, but portable source of hydrogen for filling war balloons:  $\text{CaH}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + 2\text{H}_2$ .

**Calcium Chloride  $\text{CaCl}_2$ .** — Calcium-ion is present in small amount in sea-water, and hence compounds containing calcium chloride, such as tachydrate  $\text{CaCl}_2 \cdot \text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ , are found in salt deposits. The salt, for which there is no extensive commercial application (*cf.* p. 688), is formed in large quantities as a by-product in several industrial operations. Thus, it arises in the liberation of ammonia from ammonium chloride by the action of lime, in the manufacture of potassium chlorate (p. 481), and in the Solvay soda process (p. 688). By evaporation of any solution the **hexahydrate** of the salt,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , is obtained in large, deliquescent, six-sided prisms. On account of the great concentration of a saturated solution of this compound, the solid and solution do not reach a condition of equilibrium with ice (*cf.* p. 200) until the temperature has fallen to  $-50^\circ$ . The freezing mixture is best made with the hydrate, and not with the anhydrous salt, as the latter gives out much heat in becoming hydrated (dissolving). The former absorbs heat in liquefying, as all solids do.

There are several other hydrates of calcium chloride containing less than  $6\text{H}_2\text{O}$ , and those containing less water have lower aqueous tensions (*cf.* p. 153) than have those containing more. By elevating the temperature, however, it is easy to raise the aqueous tension even of the monohydrate until it exceeds the partial pressure of water vapor in ordinary moist air, and so to drive out the water. To perform this rapidly, a temperature of over  $200^\circ$  is required. The partially dehydrated calcium chloride  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  forms a porous mass which is used in chemical laboratories for drying gases and liquids. Usually the dehydration is left incomplete, as, at the temperature required to complete it rapidly, some interaction with the water occurs:  $\text{CaCl}_2 + \text{H}_2\text{O} \rightarrow \text{CaO} + 2\text{HCl}$ , and a little free alkali is present in the product. When calcium chloride is used as a drying agent, it is naturally able to reduce the partial pressure of the water vapor only to the value of the aqueous tension of the hydrate which is present, and no further. Even at low temperatures the aqueous tensions of hydrates are always perceptible (*cf.* p. 152). Concentrated sulphuric acid is a more thorough drying agent than is calcium chloride, and phosphorus

pentoxide, whose hydrated form (metaphosphoric acid) has no observable aqueous tension, is better still.

Calcium chloride forms molecular compounds, not only with water, but also with ammonia  $\text{CaCl}_2 \cdot 8\text{NH}_3$  and with alcohol. For drying these substances, therefore, quicklime is employed. Hydrogen sulphide interacts with the salt, giving hydrogen chloride, which renders the gas impure. This gas is therefore dried with phosphorus pentoxide.

**Calcium Fluoride  $\text{CaF}_2$ .** — This compound occurs in nature as fluorite or fluor-spar  $\text{CaF}_2$ . It crystallizes in cubes, is insoluble in water, and when pure is colorless. Natural specimens often possess a green tint or show a violet fluorescence. It is formed as a precipitate when a soluble fluoride is added to a solution of a salt of calcium.

Fluorite is used in the etching of glass, as the source of the hydrogen fluoride (p. 281). It is easily fusible, as its name indicates (Lat. *fluere*, to flow), and is employed in metallurgical operations, for the purpose of lowering the melting-point (or freezing-point, which is the same thing, cf. p. 144) of the slag (p. 653), and so facilitating the separation of the latter from the metal.

**Calcium Carbonate  $\text{CaCO}_3$ .** — This compound is found very plentifully in nature. Limestone is a compact, indistinctly crystalline variety, while marble is a distinctly crystalline form. Chalk\* is a deposit consisting of the calcareous parts of minute organisms; and egg-shells, oyster-shells, coral, and pearls are other varieties of organic origin.† A laminated kind of limestone found at Solnhofen is used for lithographic work. Calcite and Iceland spar (Ger. *spalten*, to split) are pure crystallized calcium carbonate. The former occurs in flat rhombohedrons, or in pointed, six-sided crystals (Fig. 68, p. 172) known as scalenohedrons ("dog-tooth" spar) belonging to the same system. All the crystals split with ease parallel to three planes of cleavage, giving rhombohedrons of the shape shown in Fig. 69 (p. 173), but this nearly cubical form is itself seldom found in nature. An entirely different crystallized variety is known as aragonite. This belongs to the rhombic system, although complex crystals ("twins") of hexagonal outline constitute the most familiar specimens. Aragonite, when heated gently, resolves itself into a mass of minute

\* Blackboard "crayon" is usually made of gypsum, and not of chalk.

† The hard coverings of crustacea and insects are not made of this substance, but of an organic material called **chitin**.

ystals of calcite, and the latter is the more stable form of the substance. When calcium carbonate is produced by precipitation it is first amorphous but slowly becomes crystalline. In cold liquids the resulting crystals are calcite; but in warm solutions the less stable form, that of aragonite, is first assumed.

When heated, calcium carbonate dissociates, giving carbon dioxide and quicklime



At ordinary temperatures the decomposition is imperceptible. On the contrary, atmospheric carbon dioxide, in spite of its very low partial pressure, combines with quicklime, giving "air-slaked" lime. As the temperature rises, however, the tension of carbon dioxide coming from the carbonate increases, and has a fixed value for each temperature. If it is continually allowed to escape, so that the maximum pressure is not reached, the whole of the salt eventually decomposes. If, on the other hand, the gas is confined, the system reaches a condition of equilibrium. Attempts to increase the pressure on the gas beyond the dissociation pressure proper to the existing temperature, result in recombination. At 700° the pressure is only 25 mm., at 900° it reaches an atmosphere, and at 950° two atmospheres. The phenomenon is similar to the dissociation of barium peroxide (p. 82) and to the evaporation of a liquid (p. 145).

Limestone is used in the manufacture of quicklime (*q.v.*) and of glass. It is employed largely as a flux in metallurgy, when minerals rich in silica are brought into fusible form by the production of calcium silicate  $\text{CaSiO}_3$ . Large amounts also find application as building-stone.

Limestone is soluble in water containing carbonic acid, giving calcium bicarbonate  $\text{Ca}(\text{HCO}_3)_2$  (p. 141, also see p. 722). By solution of limestone, caves are often formed. Conversely, subterranean water containing the bicarbonate, when it reaches such a cavern, loses carbon dioxide and deposits calcium carbonate as stalactites or columns hanging from the ceiling. The drippings form stalagmites on the floors.

*The Phase Rule, a Method of Classifying all Systems in Equilibrium.* — The formal resemblance that we have just shown to exist between the modes of behavior of a system composed of water and water-vapor in physical equilibrium, on the one hand, and of a system made up of calcium oxide, carbon dioxide, and undecom-



posed calcium carbonate in chemical equilibrium, on the other, is not a coincidence. A study of all kinds of systems in equilibrium shows that their different modes of behavior are limited in variety and can be classified in a very simple way.

The categories used for classification are: (1) the **independent components** in the system, and their number; (2) the distinct, physically separable parts or **phases** (p. 192) of the system, and their number; and (3) the **conditions** — temperature, pressure, and concentration; and (4) the **degree of variability in the conditions** which is possible **without the occurrence of a change in the number of the phases**.

The mode of employment of these three categories may be illustrated in the order of their mention:

1. In the water and water-vapor system, water is the *only component*. In the calcium carbonate system, the independent components are *two* in number, calcium oxide and carbon dioxide.

2. In the water and water-vapor system there are *two phases*, the liquid phase and the vapor phase. In the calcium carbonate system there are *three phases* — two solid phases, the carbonate and oxide, and one gaseous phase, the carbon dioxide.

3. In the water and water-vapor system either the temperature or the pressure may be altered, within certain limits, at will. But, whichever one of these two conditions it be that is thus changed, *the preservation of the two phases* will at once require a simultaneous modification in the other condition, of such a nature as will suit the new value of the first. Thus, if the pressure upon the vapor is raised, the vapor phase will be destroyed (p. 146) unless the temperature is simultaneously elevated to a certain definite point (p. 146). Similarly, if the temperature is raised, the liquid phase will pass into vapor unless a sufficient increase in the pressure is simultaneously effected. There is therefore one, and only one degree of variability in the conditions — the system is **univariant**. The experimenter has only *one* free choice, and after he has made this choice, the other condition necessary to preserve the number of phases is determined by the system. By a study of the calcium carbonate system, as described above, it will be seen that it also is a univariant system.

A partial generalization of these results leads to the conclusion that when the number of the phases exceeds the number of the components by *one*, the system is univariant. Additional illustrations are now required for reaching a still more general statement.

If ice be added to the water and water-vapor system, and the system be allowed to reach equilibrium with all three phases present,

we find on analyzing as before: one component (water), three phases (solid, liquid, and gaseous), and no variability in the system. *Neither* temperature *nor* pressure may be altered without ensuing disappearance of one or other of the three phases. This system is therefore **invariant**.

It thus appears that with an equal number of components, the more phases we have, the more restricted are the possibilities of change in the conditions. When the number of phases equals the number of components, the system is bivariant; when the number of phases exceeds the number of components by one, the system is univariant; when the number of phases exceeds the number of components by two, the system is invariant, and, in general,

$$\text{Components} + 2 = \text{Phases} + \text{Variable conditions.}$$

The law, of which this equation is the most compact expression, is known as the **phase rule**, and was first formulated by Willard Gibbs, of Yale University. It applies to physical and chemical equilibria without distinction, and involves no consideration of molecules or atoms.

Thus, the formal resemblance between the dissociation phenomena exhibited by calcium carbonate and other compounds, on the one hand, and the behavior of a liquid in contact with its vapor on the other, is due simply to the fact that in each case the number of phases exceeds the number of components by one. This will be found to hold in all cases where there is, at each temperature, a constant dissociation pressure. A decomposing hydrate, for example, furnishes such a case. The system is made up of one gaseous phase (water-vapor) and two solid phases (the hydrate, and the anhydrous substance or a lower hydrate). It has three phases and two components (water and the anhydrous substance), and is, therefore, univariant.

Again, when we have a sharp transition-point at a fixed temperature, that is, a unique temperature at which alone several different states of aggregation of a substance can co-exist (p. 144), the system is always invariant. Thus, ice and water (and vapor) co-exist at the melting-point of ice: three phases and one component. Again, at 96° two solid forms of sulphur (p. 412) co-exist with sulphur vapor. In these cases the change which takes place at the transition point is purely *physical*. Analogous cases in which the change is a *chemical* one are equally familiar. The decahydrate of sodium carbonate decomposes (p. 689) above 35.2°. At this temperature the decahydrate and the monohydrate co-exist with the saturated solution

and water-vapor: four phases and two components. The system is, therefore, invariant. The cases of gypsum (see p. 718) and sodium sulphate (p. 193) are similar.

In the case of barium peroxide, it has been found by Hildebrand that, as a given specimen decomposes at a fixed temperature, it does *not* give a constant pressure of oxygen, but a continuously diminishing pressure. This shows that the two solid phases,  $\text{BaO}$  and  $\text{BaO}_2$ , are not independent of one another, otherwise the latter would give the same pressure of oxygen until it was all decomposed. These substances must be soluble in one another, giving a solid solution, and therefore a single phase. This introduces a second variable, namely the concentration of this solid solution. The same thing has been observed with the carbonates, so that  $\text{CaO}$  and  $\text{CaCO}_3$  are mutually soluble, and the dissociation pressure is not strictly constant, but varies with the proportions in which the solids are present, as well as with the temperature.

**Calcium Oxide  $\text{CaO}$ .** — Pure oxide of calcium (**quicklime**) may be made by ignition of pure marble or calcite. For commercial purposes limestone is converted into quicklime in kilns (Fig. 145).

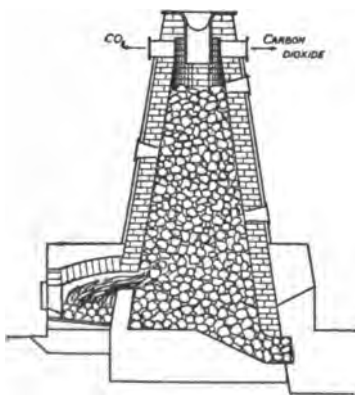


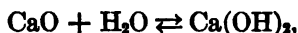
FIG. 145.

In the United States the "long-flame" process, in which the kiln is first charged with limestone and a fire is then kindled in a cavity left at the bottom, is the one most commonly used. Elsewhere, the limestone and coal are thrown, in alternate layers, into the kiln, and the products are withdrawn at the bottom. The latter, the "short-flame" method, demands less fuel, since the operation is continuous, and the structure is never allowed to cool, but the quicklime is mixed with the ash of the coal. In both cases, the flames and heated gases from the fire pass between the pieces of limestone, and the carbon dioxide liberated is carried off by the draft. When the gas is to be used in the Solvay process or in the refining of sugar, coke (smokeless), instead of coal, is employed as the fuel. As low a temperature as possible is used. A high temperature causes impurities in the

limestone (*e.g.*, clay) to interact with the quicklime, giving fusible silicates, which fill the pores and interfere with the subsequent slaking with water. Since the change is reversible, if the gas lingers in the kiln (at 760 mm. pressure), a temperature over  $900^{\circ}$  is required to drive the action forward (p. 705). Hence, a good draft, which removes the gas as fast as it is formed, permits the use of a lower temperature.

Pure calcium oxide is a white, porous solid. It is infusible even in the oxyhydrogen flame, but may be melted and boiled in the electric arc. It is not reducible by sodium, or by carbon excepting at the temperature of the electric furnace.

**Calcium Hydroxide  $\text{Ca}(\text{OH})_2$ .** — When water is poured upon quicklime it is first absorbed into the pores mechanically. The chemical union by which the hydroxide is formed:



proceeds slowly. When it is complete, the product is a fine powder occupying a larger volume than the original materials. Much heat is evolved, and part of the water is driven off as steam. The action is reversible, and at a high temperature the hydroxide can be dehydrated. Quicklime from pure limestone slakes easily, and is known as "fat" lime. That made from material containing clay or magnesium carbonate is "poor" lime. The latter slakes slowly and often incompletely, and, when used for mortar, does not harden so satisfactorily.

Calcium hydroxide is slightly soluble in water (*limewater*), 600 parts of water dissolving 1 part of the hydroxide at  $18^{\circ}$ , about twice as much water being required at  $100^{\circ}$ . The solution, relatively to its concentration, is strongly alkaline. On account of its cheapness, this substance is used by manufacturers in almost all operations requiring a base, and it thus occupies the same position amongst bases that sulphuric acid does amongst acids. When the presence of much water is unnecessary or undesirable, a suspension of the solid hydroxide in the saturated solution ("milk of lime"), or even a paste, is employed. In such cases, as in the manufacture of caustic alkalis (p. 666), the action takes place with the part which is at the moment in solution, and proceeds through the continual readjustment of a complex set of equilibria. Caustic lime is employed in the manufacture of alkalis (p. 666), bleaching powder, and mortar (see

below), the removal of the hair from hides in preparation for tanning, the softening of water, and as a whitewash.

**Mortar.** — Mortar is made by mixing water with slaked lime and a large proportion of sand. The "hardening" process consists in an interaction of the carbon dioxide of the air with the calcium hydroxide:



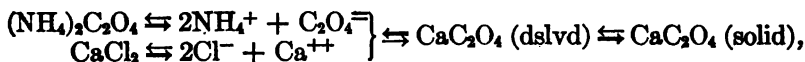
After the superficial parts have been changed, the process goes on very slowly, and many years are required before the deeper layers have been transformed. The minute crystals of calcium carbonate which are formed are interlaced with the sand particles, and a rigid mass is finally produced. The sand is useful in two ways. In the first place, it makes the whole material more porous, and so facilitates the diffusion of the gas into the interior. In the second place, since the sand is not itself altered, its presence prevents the formation of large cracks which would otherwise arise from the shrinkage that accompanies the formation of the carbonate. The "hardening" does not begin until the excess of water used in making the mortar has evaporated, and hence ordinary mortar is unsuitable for use in damp places such as cellars.

**Calcium Oxalate  $\text{CaC}_2\text{O}_4$ .** — This salt may be observed under the microscope in the cells of many plants. It appears in the form of needle-shaped or of granular crystals. Since it is the least soluble salt of calcium, its formation is used as a test for calcium-ion. Calcium is estimated quantitatively by adding ammonium oxalate to the neutral or slightly alkaline solution of the calcium salt. The precipitate is separated by filtration, washed with water, and then heated strongly (*ignited*) in a crucible. The product weighed is calcium oxide,  $\text{CaC}_2\text{O}_4 \rightarrow \text{CaO} + \text{CO}_2 + \text{CO}$ . More often, perhaps, the oxalate is ignited with sulphuric acid, and the calcium weighed as sulphate.

**Theory of Precipitation.** — The precipitation of calcium oxalate  $\text{CaC}_2\text{O}_4$ , just referred to, is a typical one and may be used to illustrate the application of ion-product constancy (p. 698) to explaining the phenomenon. The same explanation serves for all precipitations involving double decomposition.

The first thing to be remembered is that the precipitate which we

observe, however insoluble its material may be, does not include *all* of the substance, but only the excess beyond what is required to saturate the water. **The liquid surrounding the precipitate is always a saturated solution of the substance precipitated.** If it were not so, some of the precipitate would dissolve until the liquid became saturated. Thus, for example, when we add ammonium oxalate solution to calcium chloride solution:



the liquid is a saturated solution of calcium oxalate, with the excess of this salt suspended in it as a precipitate.

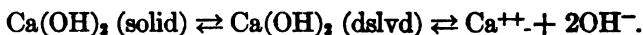
Looking at the matter from this viewpoint, we perceive the application of the rule of ion-product constancy. In this *saturated* solution (p. 698) the product of the ion-concentrations,  $[\text{Ca}^{++}] \times [\text{C}_2\text{O}_4^{=}]$ , is constant. If the original solutions had been so very dilute that, when they were mixed, the product of the concentrations of these two ions had *not* reached the value of this constant, *no precipitation would have occurred*. As a matter of fact the ion-product considerably exceeded the requisite value, and hence the salt was thrown down until the balance remaining gave the numerical value in question. The rule for precipitation, then, is as follows: **Whenever the product of the concentrations of any two ions in a mixture exceeds the value of the ion-product in a saturated solution of the compound formed by their union, this compound will be precipitated.** Naturally the substances with small solubilities, and therefore small ion-product constants, are the ones most frequently formed as precipitates.

In the case of calcium oxalate, the molar solubility (see Table) is 0.043. In so dilute a solution the substance, being a salt (p. 369), must be practically all ionized. *Each* molecule gives one ion of each kind. The molar concentrations of these ionic substances,  $\text{Ca}^{++}$  and  $\text{C}_2\text{O}_4^{=}$ , *in the solution*, when the *solid is also present*, must therefore be (practically) 0.043, *each*. The product  $[\text{Ca}^{++}] \times [\text{C}_2\text{O}_4^{=}]$  is thus equal to  $0.043 \times 0.043$  or 0.00185. If in mixing the solutions, exactly equivalent quantities were not employed, the values of the two factors will not be equal, but the *product* will in any case possess this value.

**Rule for Solution of Substances.**—The rule for solution of *any* ionogen follows at once from the foregoing considerations, and may be formulated by changing a few of the words in the rule just given:

Whenever the *product* of the concentrations of any two ions in a mixture is *less than* the value of the ion-product in a saturated solution of the compound formed by their union, this compound, if present in the solid form, will be *dissolved*. When applied to the simplest case, this rule means that a substance will dissolve in a liquid not yet saturated with it, but will not dissolve in a liquid already saturated with the same material. The value of the rule lies in its application to the less simple, but equally common cases, such as when an insoluble body is dissolved by interaction with another substance (next section).

**Applications of the Rule for Solution to the Solution of Insoluble Substances.** — So long as a substance remains in pure water its solubility is fixed. Thus, with calcium hydroxide at 18°, the system comes to rest when 0.17 g. per 100 c.c. of water (0.02 moles per liter) have gone into solution:



But if an additional reagent which can combine with either one of the ions is added, the concentration of this ion at once becomes less, the ion-product therefore tends to diminish, and further solution must take place to restore its value. Thus, if a little of an acid (giving  $\text{H}^+$ ) be added to the solution of calcium hydroxide, the union of  $\text{OH}^-$  and  $\text{H}^+$  to form water removes the  $\text{OH}^-$ , and solution of the hydroxide proceeds until the acid is used up. There are now more  $\text{Ca}^{++}$  than  $\text{OH}^-$  ions present, but the *ion-product* reaches the same value as before, and then the change ceases. If a further supply of acid is added, the removal of  $\text{OH}^-$  to form  $\text{H}_2\text{O}$  begins again. With *excess of the acid*, the only stable  $\text{OH}^-$  concentration is that which is a factor in the very minute ion-product of water,  $[\text{OH}^-] \times [\text{H}^+]$ , which is  $0.01 \times 0.01$ , or  $0.01$ . Hence, with excess of acid, the calcium hydroxide, which requires in general a much higher concentration of  $\text{OH}^-$  than this to precipitate it or to keep it out of solution, finally all dissolves.

More specifically, if we assume that the calcium hydroxide is wholly dissociated in so dilute a solution (which is nearly true), each molecule forms one ion of  $\text{Ca}^{++}$  and two ions of  $\text{OH}^-$ . That is, each mole of  $\text{Ca(OH)}_2$  gives one mole of  $\text{Ca}^{++}$  and two moles of  $\text{OH}^-$ . As the saturated solution contains 0.02 moles of the base, the molar concentration (assuming complete dissociation) of  $[\text{Ca}^{++}]$  is 0.02 and of  $[\text{OH}^-]$  is 0.04. Now, the ion-product is the product of the concentrations of all the ions formed, i.e.,  $\text{Ca}^{++}$ ,

$\text{OH}^-$ , and  $\text{OH}^-$ . The value of the product is therefore  $[\text{Ca}^{++}] \times [\text{OH}^-] \times [\text{OH}^-]$  or  $[\text{Ca}^{++}] \times [\text{OH}^-]^2$ . That is,  $0.02 \times 0.04^2 = 0.0032$ . Note that if the molecule gives two (or three) ions of the same kind, the *whole* concentration of that ion taken, and is also raised to the *second* (or third) *power*.

This particular action is a neutralization of an insoluble base. But the other kinds of actions by which insoluble ionogens pass into solution all resemble it closely, and differ only in details. The general outlines of the explanation are the same in every case. We proceed now to apply it to the common phenomenon of the solution of an insoluble salt by an acid.

**Interaction of Insoluble Salts with Acids, Resulting in Solution of the Salt.** — Calcium oxalate passes into solution when in contact with acids, especially active acids. With hydrochloric acid, it gives calcium chloride and oxalic acid, both of which are soluble:



The action of acids upon insoluble salts is so frequently mentioned in chemistry and is so important a factor in analytical operations that it demands separate discussion. This example is a typical one and may be used as an illustration.

According to the rules already explained (p. 711), calcium oxalate (or any other salt) is precipitated when the numerical value of the product of the concentrations of the two requisite ions  $[\text{Ca}^{++}] \times [\text{C}_2\text{O}_4^{=}]$  exceeds the value of the ion-product for a saturated solution of calcium oxalate in pure water, that is, exceeds 0.00185 (p. 711). When, on the contrary, the product of the concentrations of the two ions falls below the limiting value, a condition which may arise from the removal in some way either of the  $\text{Ca}^{++}$  or of the  $\text{C}_2\text{O}_4^{=}$  ions, the undissociated molecules will ionize, and the solid will dissolve to replace them until the ionic concentrations necessary for equilibrium with the molecules have been restored or until the whole of the solid present is consumed. Here the oxalate-ion from the calcium oxalate combines with the hydrogen-ion of the acid (usually an active one) which has been added, and forms molecular oxalic acid:



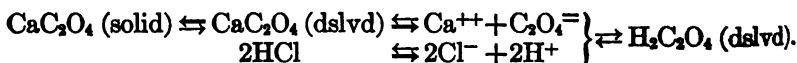
Hence, dissociation of the dissolved molecules of calcium oxalate proceeds, being no longer balanced by encounters and unions of the now



depleted ions, and this dissociation in turn leads to solution of other molecules from the precipitate.

It will be seen that the removal of the ions in this fashion can result in considerable solution of the salt only when the acid produced is a feebly ionized one. Here, to be specific, the concentration of the  $\text{C}_2\text{O}_4^{=}$  in the oxalic acid equilibrium (2) above must be less than that of the same ion in a saturated calcium oxalate solution. Now oxalic acid does not belong to the least active class of acids, and its pure solution contains a considerable concentration of  $\text{C}_2\text{O}_4^{=}$ . There is, however, a decisive factor in the situation which we have not yet taken into account. The hydrochloric acid which we used for dissolving the precipitate is a very highly ionized acid and gives an enormously greater concentration of hydrogen-ion than does oxalic acid. Hence the hydrogen-ion is in excess in equation (2), and the condition for equilibrium,  $\frac{[\text{H}^+]^2 \times [\text{C}_2\text{O}_4^{=}]}{[\text{H}_2\text{C}_2\text{O}_4]} = K$ , will be satisfied by

a correspondingly small concentration of  $\text{C}_2\text{O}_4^{=}$ . In this particular case, therefore, the  $[\text{C}_2\text{O}_4^{=}]$  of the oxalic acid is less than that given by the calcium oxalate. The whole change, therefore, depends for its accomplishment, not only on the mere presence of hydrogen-ion, but *on the repression of the ionization of the oxalic acid by the great excess of hydrogen-ion furnished by the active acid that has been used.* As a matter of fact, we find that a weak acid like acetic acid has scarcely any effect upon a precipitate of calcium oxalate. An acid stronger than oxalic acid must be employed. The whole scheme of the equilibria is as follows:

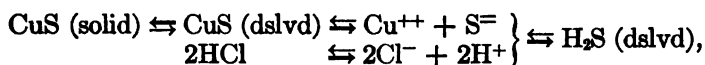


When excess of an acid sufficiently active to furnish a large concentration of hydrogen-ion is employed, the last equilibrium is then driven forward and the others follow. With addition of a weak acid, only a slight displacement occurs, and the system comes to rest again when the molecular oxalic acid has reached a sufficient concentration.

A generalization may be based on these considerations: an insoluble salt of a given acid will in general interact and dissolve when treated with a solution containing another acid, provided that the latter acid is a much more highly ionized (more active) one than the former (see below).

But even active acids frequently fail to bring salts of weak acids into solution, especially when the weak acid is itself present also.

Here the cause lies in the fact that such salts are less soluble than those of the calcium oxalate type, and give so low a concentration of the negative ion that the utmost repression of the ionization of the corresponding acid does not give a lower value for the concentration of this ion than does the salt itself. Thus, we have seen (p. 421) that even hydrochloric acid (dilute) will not dissolve a number of sulphides. For example, in the case of cupric sulphide in a solution saturated with hydrogen sulphide, the  $S^=$  factor in the solubility product  $[Cu^{++}] \times [S^=]$  remains smaller than that in the scheme defining the hydrogen sulphide equilibrium  $[H^+]^2 \times [S^=]$  even when the  $[S^=]$  factor in the latter is diminished in consequence of great addition of hydrogen-ion. In this case, the first link in the chain of equilibria:



tends so decidedly backward that only the use of concentrated acid will increase the concentration of the  $H^+$  to an extent sufficient to secure even a slight advance of the whole action. We must add, therefore, to the above rule: **provided also that the salt is not one of extreme insolubility.** This point will be illustrated more fully in connection with the description of individual sulphides (see under Cadmium).

Illustrations of the application of these generalizations are countless. Carbonic acid is made from marble (p. 573), hydrogen sulphide from ferrous sulphide (p. 419), hydrogen peroxide from sodium peroxide (p. 315), and phosphoric acid from calcium phosphate (p. 548). In each case the acid employed to decompose the salt is more active than the acid to be liberated. On the other hand, calcium oxalate and calcium phosphate (except when freshly precipitated) are insoluble in acetic acid because this acid is weaker than are oxalic and phosphoric acids. We have thus only to examine the list of acids showing their degrees of ionization (p. 367) in order to be able to tell which salts, if insoluble in water, will be dissolved by acids and, in general, what acids will be sufficiently active in each case for the purpose. In chemical analysis we discriminate between salts soluble in water, those soluble in acetic acid (the insoluble carbonates and some sulphides,  $FeS$  and  $ZnS$ , for example), those requiring active mineral acids for their solution (calcium oxalate and the more insoluble sulphides, for example), and those insoluble in all acids (barium sulphate and other insoluble salts of active acids).

The influence of solubility is shown not only by the sulphides, but

also, for example, by the sulphates. Thus, barium sulphate is not appreciably dissolved even by the most active acids (p. 440), being a salt of a rather highly ionized acid, and being itself very insoluble. Yet calcium sulphate, being much less insoluble (p. 701), is dissolved to a noticeable extent by the same acids.

***Precipitation of Insoluble Salts in Presence of Acids.***—

The converse of solution, namely, precipitation, depends upon the same conditions: an insoluble salt which is dissolved by a given acid cannot be formed by precipitation in the presence of this acid. Thus, calcium oxalate can be precipitated in presence of acetic acid, but not in presence of active mineral acids in ordinary concentrations. Cupric sulphide or barium sulphate can be precipitated in presence of any acid, but ferrous sulphide and calcium carbonate only in the absence of acids.

From this it does not follow that calcium oxalate, for example, cannot be precipitated if once an active acid has been added to the mixture. To secure precipitation, all that is necessary is to remove the excess of hydrogen-ion which is repressing the ionization of the oxalic acid. This can be done by adding a base, which removes the  $H^+$ , or even by adding sodium acetate. The acetate-ion  $C_2H_3O_2^-$  unites with the  $H^+$  to form the little ionized acetic acid, in presence of which calcium oxalate can be precipitated.

***Calcium Carbide  $CaC_2$ .***— The manufacture of this compound has been described (p. 571), and the formation of acetylene by its interaction with water has already been discussed (p. 592). The substance was discovered by Wöhler in 1862, was first prepared by the use of electrical heating by Borchers in 1891, and was made on a large scale in 1892 by Willson, a Canadian engineer. The world's production in 1912 was 300,000 tons.

***Bleaching Powder  $Ca(OCl)Cl$ .***— This substance (cf. p. 475) is manufactured by conducting chlorine into the lowest of a series of 6-8 revolving cylinders, while slaked lime is fed into the uppermost cylinder (counter-current system, see p. 687). When the transformation has reached the limit (it is never complete), some lime-dust is blown in to absorb the remainder of the free chlorine. The action is represented by the equation already given, and not by the following:



While pure lime should thus yield a product containing 49 per cent of chlorine, in practice the proportion is always less. Good bleaching powder should contain 36–37 per cent of chlorine.

That bleaching powder is a mixed salt  $\text{CaCl}(\text{ClO})$  rather than an equi-molar mixture of calcium chloride and calcium hypochlorite (equation above), which would have the same composition, is proven by the facts that the material is not deliquescent as is calcium chloride, and that calcium chloride cannot be dissolved out of it by alcohol.

Bleaching powder is somewhat soluble in water, and in solution the ions  $\text{Ca}^{++}$ ,  $\text{Cl}^-$ , and  $\text{ClO}^-$  are all present. Addition of acids causes the formation of hydrochloric and hypochlorous acids. The oxidizing and, incidentally, the bleaching properties (p. 475) of the latter are characteristic of the acidified liquid. Weak acids like carbonic acid displace the hypochlorous acid only (cf. p. 476), and hence the dry powder, when exposed to the air, has the odor of the latter substance rather than that of chlorine.

The substance is largely used by bleachers (cf. p. 477), and as a disinfectant to destroy germs of putrefaction and disease.

**Calcium Nitrate  $\text{Ca}(\text{NO}_3)_2$ .** — This salt is found in the soil (p. 525), and may best be prepared in pure form by treating marble with nitric acid and allowing the product to crystallize from the solution. Calcium nitrate forms several hydrates. The tetrahydrate  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , which forms transparent monoclinic prisms, is the one deposited at ordinary temperatures. The anhydrous salt is easily soluble in alcohol. It is used in the laboratory for drying nitrogen peroxide. When heated it decomposes (cf. p. 701), giving first oxygen and the nitrite and then nitrogen peroxide and quicklime.

**Calcium Sulphate  $\text{CaSO}_4$ .** — This salt is found in large quantities in nature. The mineral **anhydrite**  $\text{CaSO}_4$  occurs in the salt layers (see under Manganous sulphate). It contains no water of crystallization, and its crystals belong to the rhombic system. The **dihydrate**,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , is more plentiful. In granular masses it constitutes **alabaster**. When perfectly crystallized (monoclinic, Fig. 72, p. 173) it is named **gypsum** or **selenite**. The same hydrate is formed by precipitation from solutions. Its solubility is about 1 in 500 at  $18^\circ$ . Its solubility varies in an unusual manner with temperature, increasing slowly to  $38^\circ$  and then falling off.

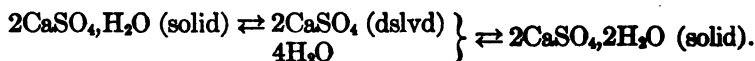
When its temperature is raised, the dihydrate quickly shows an

appreciable aqueous tension. After three-fourths of the water has escaped, a hemihydrate  $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$  remains, which shows a much smaller tension of water vapor (*cf.* p. 153).

The transition temperature at which the dihydrate passes sharply into the hemihydrate is  $107^\circ$ . It corresponds to the temperature of  $35.2^\circ$  at which the decahydrate of sodium carbonate turns into the monohydrate and water. At  $107^\circ$  both of the hydrates are in equilibrium with the solution (p. 689). Naturally this system can exist only in a tube sealed up to prevent the escape of the water.

**Plaster of paris**  $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$  is manufactured by heating gypsum until nearly all the water of hydration has been driven out. When it is mixed with water, the dihydrate is quickly re-formed and a rigid mass is produced. If, in course of manufacture, the water is all removed, or the temperature is allowed to rise much above the most favorable one (about  $125^\circ$ ), the product when mixed with water does not set quickly and is said to be "dead-burnt." In explanation of this it should be noted that natural anhydrite combines very slowly with water. Apparently good plaster of paris must contain some unchanged particles of the dihydrate which may act as nuclei. They fulfil the same rôle as the crystal which is added to a super-saturated solution (p. 193), without which crystallization may be long delayed or may even fail to take place. Probably, with moderate heating, the product is a mixture of the dihydrate and the hemihydrate with anhydrous salt, while the more rapid decomposition at higher temperatures destroys all of the first. The former mixture must be an unstable system, and the dihydrate loses water to the anhydrous salt. At ordinary temperatures, however, this transference must be very slow, and hence the property of setting is not lost by prolonged storage.

That the plaster sets, instead of forming a loose mass of dihydrate, is due to the fact that the anhydrous salt is more soluble than the dihydrate, and so a constant solution of the one and deposition of the other goes on until the hydration is complete:

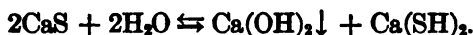


This process results in the formation of an interlaced and coherent mass of minute crystals.

Plaster of paris is used for making casts and in surgery. The setting of the material is accompanied by a slight increase in volume, and hence a very sharp reproduction of all the details in the structure

of the mold is obtained. An "ivory" surface, which makes washing practicable, is conferred by painting the cast with a solution of paraffin or stearine in petroleum ether. The waxy material, left by evaporation of the volatile hydrocarbons, fills the pores and prevents solution and disintegration of the substance by water. Stucco is made with plaster of paris and rubble, and is mixed with a solution of size or glue instead of water.

**Calcium Sulphide CaS.** — This compound is most easily made by strongly heating pulverized calcium sulphate and charcoal. The sulphate is reduced:  $4C + CaSO_4 \rightarrow CaS + 4CO$ . Calcium sulphide is meagerly soluble in water, but is nevertheless slowly dissolved in consequence of its decomposition by hydrolysis into calcium hydroxide and calcium hydrosulphide (*cf.* p. 421). It is probable that the action would be less nearly complete than it is if the reverse action were not weakened by the precipitation of the calcium hydroxide:



Since calcium sulphide is thus decomposed by water it cannot be precipitated from aqueous solution by adding a soluble sulphide, such as ammonium sulphide, to a solution of a salt of calcium. Only the soluble hydrosulphide can be formed.

Ordinary calcium sulphide, after it has been exposed to sunlight, usually shines in the dark. Barium sulphide behaves in the same way. On this account these substances are used in making luminous paint. They apparently owe this behavior to the presence of traces of compounds of vanadium and bismuth, for the purified substances are not affected in the same fashion. Since alkalies decompose proteins, moist calcium sulphide is used as a depilatory.

**Phosphates of Calcium.** — The tertiary orthophosphate of calcium  $Ca_3(PO_4)_2$ , known as phosphorite, is found in many localities, and is often derived from the bones of animals. Guano contains some of the same substance, along with nitrogen, either as organic compounds or as niter (p. 525). **Apatite**  $3Ca_3(PO_4)_2, CaF_2$ , a double salt with calcium fluoride (or chloride) is a common mineral and frequent component of rocks. The orthophosphate forms about 83 per cent of bone-ash (p. 548), and is contained also in the ashes of plants. It may be precipitated by adding a soluble phosphate to a solution of a salt of calcium.

Since it is a salt of a weak acid, and belongs to the less insoluble class of such salts, calcium phosphate is dissolved by dilute mineral acids (*cf.* p. 714), the ions  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  being formed. When a base, such as ammonium hydroxide, is added to the solution, the calcium phosphate is reprecipitated (*cf.* p. 716).

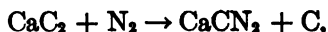
Calcium phosphate is chiefly used in the manufacture of phosphorus and phosphoric acid (p. 548), and as a fertilizer. The supply of calcium phosphate in the soil arises from the decomposition of rocks containing phosphates, and is gradually exhausted by the removal of crops. Bone-ash is sometimes used to make up the deficiency. It is almost insoluble in water, however, and, although somewhat less insoluble in natural water containing salts like sodium chloride (*cf.* p. 715), is brought into a condition for absorption by the plants rather slowly. The "superphosphate" (see below) is much more soluble.

**Primary calcium orthophosphate (superphosphate)** is manufactured in large quantities from phosphorite by the action of sulphuric acid. The unconcentrated, "chamber acid" is used for this purpose, as water is required in the resulting action. The amounts of material employed correspond to the equation:



As soon as mixture has been effected, the action proceeds with evolution of heat, and a large cake of the two hydrated salts remains. This mixture, after being broken up, dried, and packed in bags, is sold as "superphosphate of lime." The primary phosphate which it contains is soluble in water, and is therefore of great value as a fertilizer.

**Calcium Cyanamide  $\text{CaCN}_2$ .** — Calcium carbide (p. 571), when strongly heated, absorbs nitrogen, giving a mixture of calcium cyanamide and carbon:



which is sold as **nitro-lime** for use as a fertilizer. When treated with hot water, the cyanamide is hydrolyzed into calcium carbonate and ammonia:

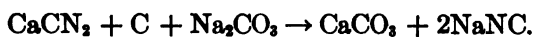


In the soil the decomposition may not be so simple, but combined nitrogen is furnished in a form that can be absorbed by plants.

At Odda (Norway) the carbide is pulverized and placed in a

cylindrical furnace (Fig. 146) holding 300–450 kg. The heat (800–1000°) is supplied by the passage of an electric current through a thin carbon rod. The nitrogen is obtained by the fractionation of liquid air and final removal of all oxygen by passage over heated copper, and is forced in under pressure. After thirty-six hours, nitrogen is no longer absorbed, and the charge is pulverized when cold.

**Sodium cyanide**  $\text{NaNC}$  is now manufactured by fusing nitro-lime with sodium carbonate:



The cyanide is extracted from the insoluble calcium carbonate with water, in which it is exceedingly soluble. Sodium cyanide has now displaced potassium cyanide in the extraction of gold from its ores.

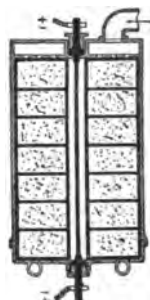


FIG. 146.

**Nutrition and Fertilization of Crops.** — The plant constructs its cellulose, starch, or sugar, and secures the carbon-part of all its organic contents from the carbon dioxide of the air (p. 579). The water (90–95 per cent of the total weight of the plant) comes from the soil and brings up in solution the other elements required. All soils are able to supply sufficient magnesium, calcium, and iron, as bicarbonates. But the soil may lack: sulphur, absorbed as sulphates; nitrogen, absorbed chiefly as nitrates, but occasionally as salts of ammonium; potassium, as sulphate, chloride, or nitrate; and phosphorus, as soluble phosphates. The soil may be originally deficient in one or more of these necessary plant foods, or the supply may have been exhausted by repeated cropping. Every crop permanently removes certain quantities. For example, in the case of nitrogen, which is required to form proteins that enter largely into the fruit (*i.e.*, usually, the edible part), each crop of Indian corn (45 bushels) removes 63 pounds per acre, a crop of cabbage (15 tons) removes 100 pounds per acre, clover hay (2 tons) 82 pounds, and wheat (15 bushels) 31 pounds. When the store in the soil becomes meager, the crops become poor, and finally cost more for labor than they are worth.

Thus, crops have to be fed, just like cattle. Moreover, the elements must be furnished in soluble form (*cf.* pp. 559, 580, 627). Fertilizers containing potassium (pp. 662, 674) and phosphorus (p. 559) must be used, when the soil is deficient in these elements.



The nitrogen fertilizers we have mentioned are sodium nitrate (p. 685), calcium nitrate (p. 525), ammonium sulphate (p. 516), guano and manure (p. 525), "tankage" and ground bones from slaughter houses, calcium cyanamide (p. 720), and finally the nitrates from bacterial decomposition of root nodules (p. 515). That systematic use of fertilizers does influence the crops is indicated by the results of cultivation of land which, but for fertilization, would long since have become almost valueless. The wheat crop per acre, being the average of ten successive years is: Denmark 40 bushels, Great Britain 33, Germany 29, United States 14.

**Hard Water.** — As we have seen (pp. 576, 705), limestone (solubility, 0.013 g. per liter), magnesium carbonate (sol'ty 1 g. per liter), and iron carbonate, although very insoluble, are acted upon by the carbonic acid in natural waters, giving bicarbonates which are roughly about thirty times as soluble. When the water is boiled, the actions (p. 576) are reversed, and the carbonates are reprecipitated. These bicarbonates constitute **temporary hardness**, and their decomposition produces "fur" in a kettle and boiler crust in a boiler.

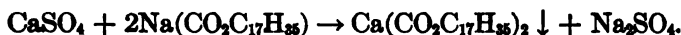
The sulphates of calcium (sol'ty 2 g. per liter) and of magnesium (sol'ty 354 g. per l.) are also commonly found in natural waters. These salts are not affected by mere boiling (as distinct from evaporation) and so, along with magnesium carbonate (1 g. per l.) and calcium carbonate (0.013 g. per l.) give **permanent hardness** to the water.

Hardness is estimated in "degrees." In France, and commonly in the laboratory, 1 part of  $\text{CaCO}_3$  (or its equivalent of other salts) per 100,000 (0.01 g. per liter) constitutes one degree. In the United States one degree is 1 grain per gallon of 58,333 grains (0.017 g. per l.). In Britain one degree is 1 grain per gallon of 70,000 grains (0.014 g. per l.). Well water, originating in chalk or limestone formations, may have 37° (Fr.) or more of hardness.

**Damage Due to Hardness in Water.** — When hard water is continually fed into a **steam boiler** and only steam comes out, naturally the salts accumulate and produce in time a heavy boiler crust, which settles on the tubes. Being a poor conductor of heat compared with iron, this crust, if one-fourth of an inch thick, will increase the consumption (and cost) of fuel by 50 per cent. In

addition, the iron, not being in direct contact with water, is heated to a higher temperature, and may even become red hot. It thus oxidizes more quickly on the outside, and displaces hydrogen from water (or steam) on the inside (p. 116), thus changing on both sides gradually into the brittle magnetic oxide  $\text{Fe}_3\text{O}_4$ . If the crust is not removed, or prevented (see below), the life of the boiler is greatly shortened, and a serious explosion may even occur.

In **washing**, in the household or laundry, much soap is wasted before the necessary lather is secured. The soap, for example, the sodium stearate (p. 620), gives magnesium and calcium stearates, which are insoluble, forming a curd:



The permanent solution of soap, required for washing, does not begin to be formed until all the hardness has thus been precipitated. Hence, according to the equation, with  $1^\circ$  (U. S.) hardness, 100 gallons (U. S.) of water should use up 0.075 pounds of soap ( $1^\circ$  Brit. and 100 gal. Brit., 0.075 lb.). In point of fact, however, the colloidal calcium salts adsorb and carry down with them more than an equal amount of undecomposed soap. Hence, actual measurement shows that, with  $1^\circ$  (U. S. or Brit.) of hardness, 100 gallons (U. S. or Brit.) of water really destroy 0.17 pounds of soap. Thus, with  $35^\circ$ , no less than 6 pounds of soap per 100 gallons are wasted before the part of the soap that is to do the work begins to dissolve.

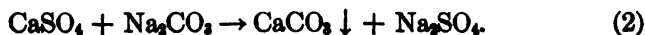
**Treatment of Hard Water.**—The temporary hardness can be removed by boiling the water, or using some preheating arrangement in connection with the boiler (stationary engines only).

**Temporary hardness** is commonly removed, on a large scale, by adding *slaked lime* (made into milk of lime) in *exactly the quantity* shown by an analysis of the water to be required, and stirring for a considerable time:



The bicarbonate is neutralized and all the lime precipitated. The latter is removed by filtration.

**Permanent hardness** is not affected by slaked lime, but is precipitated by adding sodium carbonate in the necessary proportion:



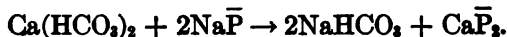
When both kinds of hardness are present, crude caustic soda (sodium hydroxide) may be employed. It neutralizes the bicarbonate, precipitating  $\text{CaCO}_3$ :



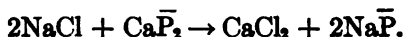
and giving sodium carbonate. The latter then acts as in equation (2).

Instead of this, the treatments indicated in equations (1) and (2) may be applied in combination (Porter-Clark process).\*

In the **permutite process**, the water is simply filtered through sodium silico-aluminate (permutite  $\text{NaP}$ , an artificial zeolite), which is supplied in the form of a coarse, insoluble sand. The calcium, etc., in the water is exchanged for sodium, which does no harm:



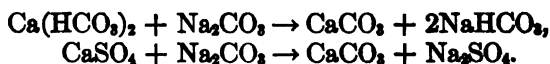
After twelve hours' use, the permutite is covered with 10 per cent salt solution, and allowed to remain for the other twelve hours of the day, when it is ready for employment once more:



Only salt, which is inexpensive, is consumed, and calcium chloride solution is thrown away. Permutite removes magnesium, iron, manganese, and other elements in the same way. The life of a charge is said to be over twenty years.

**Hard Water in the Laundry.**—As we have seen (p. 620), soap will soften water, but the calcium and magnesium salts of the soap acids, which are precipitated, are sticky, and soil the goods being washed. Other substances that soften water, not only give non-adhesive precipitates, but are also much cheaper, and an attempt is generally made to utilize them. The use of slaked lime is impracticable on a small scale.

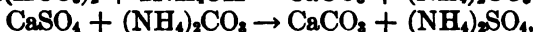
**Washing soda**  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  is added to precipitate both kinds of hardness:



\* So far as the hardness is due to magnesium bicarbonate, a double proportion of lime must be added to precipitate the magnesium as hydroxide (sol'ly 0.01 g. per l.), because the carbonate is too soluble (1 g. per l.).

The small amounts of salts of sodium which remain in the water have no action on soap.

*Household Ammonia*  $\text{NH}_4\text{OH}$  acts like sodium hydroxide (p. 724):



except that it will *not* precipitate magnesium-ion.

*Borax*  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  (p. 639) is hydrolyzed and the sodium hydroxide in its solution acts as already (p. 724) described.

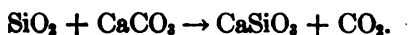
The supposed bleaching or whitening action of borax or soda is a myth; these salts *prevent staining by the iron* in the water. They simply precipitate the iron, present as  $\text{Fe}(\text{HCO}_3)_2$ , which almost all waters contain, as  $\text{FeCO}_3$  *before* the goods are put in. This precipitate is easily washed out in rinsing. The palmitate, etc., of iron, however, which the soap itself would throw down, is sticky and adheres to the cloth. The air subsequently oxidizes it (see p. 801) and gives hydrated ferric oxide (rust), which is brownish-red.

It is evident that, properly to achieve their purpose, the soda and borax must be added, must be completely dissolved, and must be allowed to produce the precipitation of  $\text{FeCO}_3$ ,  $\text{CaCO}_3$ , etc., all *before* the soap (or the goods) is introduced. If the soap is dissolved before or with the soda, it will take part in the precipitation, and give sticky particles containing the iron and calcium salts of the soap acids.

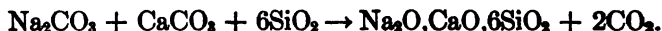
The soda, borax, and ammonia do not themselves remove dirt—that is done by the dissolved soap (p. 623). With the help of rubbing, however, they do emulsify and remove animal or vegetable oil and grease, but not mineral oil (p. 625), when these happen to be on the goods. But soap alone will do this also, and remove mineral oil as well.

*Washing powders* are, or ought to be, mainly sodium carbonate, mixed with more or less pulverized soap.

**Calcium Metasilicate**  $\text{CaSiO}_3$ .—This salt forms the mineral wollastonite, which is rather scarce, and enters into the composition of many complex minerals, such as garnet, mica, and the zeolites. It may be made by precipitation from a solution of sodium metasilicate (p. 634), or by fusing together powdered quartz and calcium carbonate:



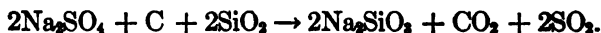
**Glass.** — Common glass is a complex silicate of sodium and calcium, or a homogeneous mixture of the silicates of these metals with silica. It has a composition represented approximately by the formula  $\text{Na}_2\text{O}, \text{CaO}, 6\text{SiO}_2$ , and is made by melting together sodium carbonate, limestone, and pure sand:



For the most fusible glass, a smaller proportion of quartz is employed. This variety is known as **soda-glass**, or, from its easy fusibility, as **soft glass**. First, the materials are heated to a temperature high enough to produce chemical action without bringing about complete melting. This permits the ready escape of the gas. Then the temperature is raised to about  $1200^\circ$  until fusion is complete and all the bubbles have escaped. Finally, the crucible and its contents are allowed to cool to  $700\text{--}800^\circ$  to permit the latter to acquire the viscosity required for working.

Plate-glass is made by rolling the material into large sheets and polishing the surfaces until they are plane. Window-glass is prepared by blowing bulbs of long cylindrical shape, and ripping them down one side with the help of a diamond. The resulting curved sheets are then placed on a flat surface in a furnace and are there allowed to open out. Beads are made, chiefly in Venice, by cutting narrow tubes into very short sections and rounding the sharp edges by fire. Ordinary apparatus is made of soft soda-glass, and hence when heated strongly it tends to soften and also to confer a strong yellow tint (*cf.* p. 692) on the flame. In all cases the articles are annealed by being passed slowly through a special furnace in which their temperature is lowered very gradually. Glass which has been suddenly chilled is in a state of tension and breaks easily when handled.

Bottles are made with impure materials, and owe their color chiefly to the silicate of iron which they contain. In making cheap glass, sodium sulphate is substituted for the more expensive carbonate. In this case powdered charcoal or coal is added to reduce the sulphate:



Soft glass is partially dissolved by water. When powdered glass is shaken with water, sodium silicate dissolves in amount sufficient to give an alkaline reaction with phenolphthalein (*cf.* p. 143).

Bohemian, or **hard glass**, is much more difficult to fuse than soda-glass, and is also much less soluble in water. It is made by substituting potassium carbonate for sodium carbonate. Specially

insoluble glass, for laboratory use, such as *Jena* and *non-sol* glass, is made with boric anhydride  $B_2O_3$ , in addition to silica, and some zinc oxide, so that it contains borates as well as silicates. When lead oxide is employed instead of limestone, a soda-lead glass, known as *flint glass*, is produced. This has a high specific gravity, and a great refracting power for light, and is employed for making glass ornaments. By the use of grinding machinery, *cut glass* is made from it. Engraving on glass is done with the sand blast.

**Colored glass** is prepared by adding small amounts of various oxides to the usual materials. The oxides combine with the silica, and produce strongly colored silicates. Thus, cobalt oxide gives a blue, chromium oxide or cupric oxide a green, and uranium a yellow glass. Cuprous oxide, with a reducing agent, and compounds of gold, give the free metals, suspended in colloidal form in the glass, and confer a deep-red color upon it. Milk-glass contains finely powdered calcium phosphate or cryolite in suspension, and white enamels are made by adding stannic oxide.

Glass is a typical amorphous substance (*cf.* p. 154). From the facts that it has no crystalline structure, and that it softens gradually when warmed, instead of showing a definite melting-point, it is regarded as a supercooled liquid of extreme viscosity. Most single silicates crystallize easily, and have definite freezing- (and melting-) points. Glass may be regarded as a solution of several silicates. When kept for a considerable length of time at a temperature insufficient to render it perfectly fluid, some of its components crystallize out, the glass becomes opaque, and "devitrification" is said to have occurred. The absence of such changes in cold glass may be attributed to that general hampering of all molecular movements and interactions which is characteristic of low temperatures. The word "crystal" popularly applied to glass is thus definitely misleading. See quartz-glass (p. 634).

**Calcium-ion  $Ca^{++}$ : Analytical Reactions.** — Ionic calcium is colorless. It is bivalent, and combines with negative ions. Many of the resulting salts are more or less insoluble in water. Upon the insolubility of the carbonate, phosphate, and oxalate are based tests for calcium-ion in qualitative analysis (see p. 732). The presence of the element is most easily recognized by the brick-red color its compounds confer on the Bunsen flame, and by two bands — a red and a green one — which are shown by the spectroscope (p. 676).

## STRONTIUM SR

The compounds of strontium resemble closely those of calcium, both in physical properties and in chemical behavior.

**Occurrence.** — The carbonate of strontium  $\text{SrCO}_3$  is found as **strontianite** (Strontian, a village in Argyleshire), and is isomorphous with aragonite. The sulphate, **celestite**  $\text{SrSO}_4$ , is more plentiful. It shows rhombic crystals which are isomorphous with those of anhydrite, often have a blue color, and are commonly associated with native sulphur in specimens from Sicily. The metal may be isolated by electrolysis of the molten chloride.

**Compounds of Strontium.** — The compounds are all made from the natural carbonate or sulphate. The former may be dissolved directly in acids, and the latter is first reduced by means of carbon to the sulphide, and then treated with acids.

**Strontium chloride**  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ , made in one of the above ways, is deposited from solution as the hexahydrate. The **nitrate**  $\text{Sr}(\text{NO}_3)_2$  comes out of hot solutions in octahedrons which are anhydrous. From cold water the tetrahydrate is obtained (see under Manganous sulphate). The anhydrous nitrate is mixed with sulphur, charcoal, and potassium chlorate to make "red fire." The **oxide**  $\text{SrO}$  may be secured by igniting the carbonate, but on account of the low dissociation tension of the compound it is obtained with greater difficulty than is calcium oxide from calcium carbonate. It is made by heating the nitrate or hydroxide.

**Strontium hydroxide**  $\text{Sr}(\text{OH})_2$  is made by heating the carbonate in a current of superheated steam:  $\text{SrCO}_3 + \text{H}_2\text{O} \rightarrow \text{Sr}(\text{OH})_2 + \text{CO}_2$ . This action takes place more easily than does the mere dissociation of the carbonate, because the formation of the hydroxide liberates energy, and this partially compensates for the energy which has to be provided to decompose the carbonate (*cf.* p. 278). The lowering of the partial pressure of the carbon dioxide by the steam also contributes to the result (*cf.* p. 709).

The hydrate crystallizes from water as  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , and is employed in separating crystallizable sugar from molasses. By evaporation of the extract from the sugar-cane or beet-root, as much of the sugar as possible is first secured by crystallization. Then the molasses which remains is mixed with a saturated solution of strontium hydroxide. The resulting precipitate of sucrate of strontium,  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{SrO}$ , or  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{SrO}$ , is separated by a filter-press, made

into a paste with water, and treated with carbon dioxide. A second filtration parts the insoluble carbonate of strontium from the solution of sugar, and the latter is evaporated and allowed to crystallize. Calcium hydroxide, which gives a tricalcium sucrate, is often employed in the same way.

**Strontium-ion**  $\text{Sr}^{++}$  is bivalent, and gives insoluble compounds with carbonate-ion, sulphate-ion, and oxalate-ion. The presence of strontium is recognized by the carmine-red color which its compounds give to the Bunsen flame (see also p. 732). Its spectrum shows several red bands and a very characteristic blue line.

### BARIUM BA

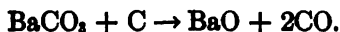
The physical and chemical properties of the compounds of barium recall those of strontium and calcium. All the compounds of barium which are soluble in water, or can be brought into solution by the weak acids of the digestive fluids, are **poisonous**.

**Occurrence.** — Like strontium, barium is found in the form of the carbonate, **witherite**  $\text{BaCO}_3$ , which is rhombic and isomorphous with aragonite, and the sulphate  $\text{BaSO}_4$ , **heavy-spar** or **barite** (Gk. *βαρύς*, heavy), which is rhombic and isomorphous with anhydrite. The density of the sulphate is 4.5, while that of other compounds of the light metals does not generally exceed 2.5. The free metal, which is silver-white, may be obtained by electrolysis of the molten chloride.

The compounds are made by treating the natural carbonate with acids directly, or by first reducing the sulphate with carbon to sulphide, or converting the carbonate into oxide, and then treating the products with acids.

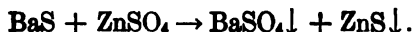
**Barium Carbonate**  $\text{BaCO}_3$ . — The precipitated form of the carbonate is made by adding sodium carbonate to the aqueous extract from crude barium sulphide (*q.v.*). The compound is also obtained by fusing pulverized barite with excess of sodium carbonate, and dissolving the sodium salts out of the residue.

This carbonate demands a high temperature (about  $1500^\circ$ ) for the attainment of a sufficient dissociation tension, and is apt then to be partially protected from decomposition by the melting of the oxide. It is therefore heated with powdered charcoal (*cf.* p. 577):



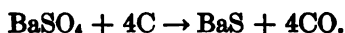


**The Sulphate and Sulphide.** — The natural sulphate  $\text{BaSO}_4$  is the source of many of the compounds of barium. The precipitated sulphate, made by adding sulphuric acid to the aqueous extract from barium sulphide, is used in making white paint ("permanent white"), in filling paper for glazed cards, and sometimes as an adulterant of white lead. A mixture of barium sulphate and zinc sulphide  $\text{ZnS}$ , prepared in a special way, is called **lithopone**:

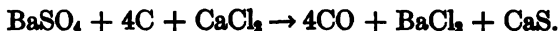


Made into paint, it has greater covering power than white lead, does not darken with hydrogen sulphide as does the latter, and is non-poisonous. The salt is highly insoluble in water and is hardly at all affected by aqueous solutions of chemical agents. It is somewhat soluble in hot, concentrated sulphuric acid, and the solution yields crystals of a compound  $\text{BaSO}_4 \cdot \text{H}_2\text{SO}_4$ , or  $\text{Ba}(\text{HSO}_4)_2$ . Calcium and strontium sulphates behave in the same way. All three compounds are decomposed by water, and give the insoluble sulphates.

**Barium sulphide**  $\text{BaS}$ , like the sulphides of calcium and strontium (p. 421), is slightly soluble in water, but slowly passes into solution owing to hydrolysis and formation of the hydroxide and hydrosulphide. It is made by heating the pulverized sulphate with charcoal:



**The Chloride and Chlorate.** — The chloride  $\text{BaCl}_2$  is generally manufactured by heating the sulphide with calcium chloride. The whole treatment of the heavy-spar is carried out in one operation:

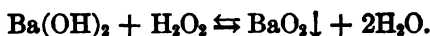


By rapid extraction with water, the chloride can be separated from the calcium sulphide before much decomposition of the latter (cf. p. 687) has taken place. Barium chloride crystallizes in rhombic tables as a dihydrate  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ . Aside from the difference in composition, this compound differs from the ordinary hydrated chlorides of calcium and strontium in being non-hygroscopic and in being capable of dehydration by heat without the formation of any hydrogen chloride (cf. p. 655).

**Barium chlorate**  $\text{Ba}(\text{ClO}_3)_2$  is made by treating the precipitated barium carbonate with a solution of chloric acid. It is deposited in beautiful monoclinic crystals, and is used with sulphur and charcoal in the preparation of "green fire."

**The Oxides and Hydroxide.** — The oxide of barium  $\text{BaO}$  is manufactured from the carbonate (see above) or sulphide. In the latter case, moist carbon dioxide is passed over the sulphide, and the resulting carbonate is then treated with steam. It may be obtained in pure form by heating the nitrate. The oxide unites vigorously with water to form the hydroxide. When heated in a stream of air or oxygen it gives the dioxide  $\text{BaO}_2$ . This change and its reversal constitute the basis of Brin's process for obtaining oxygen from the air (p. 82). To protect the oxide from conversion into the carbonate and hydrate, which are not decomposable at the temperature employed, the air must be carefully purified from carbon dioxide and moisture (cf. p. 685).

**Barium peroxide**  $\text{BaO}_2$ , when made by union of oxygen with the monoxide, is a compact gray mass. A hydrated form is thrown down as a crystalline precipitate when hydrogen peroxide solution is added to a solution of barium hydroxide:



The crystals have the formula  $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ . Similar hydrates of the peroxides of strontium and calcium may be made in the same way. In all three cases the pure peroxides are obtained as white powders by removal of the water of hydration by very gentle heating *in vacuo* (cf. p. 484). The peroxides of strontium and calcium are not formed by direct union of oxygen with the oxides. Barium peroxide is used in the manufacture of hydrogen peroxide (p. 317).

**Barium hydroxide**  $\text{Ba}(\text{OH})_2$ , is the most soluble of the hydroxides of this group, and gives, therefore, the highest concentration of hydroxide-ion. The solution is known as "baryta-water." It is also the most stable of the three hydroxides, and may be melted without decomposition. A hydrate  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  crystallizes on cooling a saturated solution. It is much used in quantitative analysis for making standard alkali-solutions. Solutions of sodium or potassium hydroxide may acquire varying proportions of carbonate by the action of carbon dioxide from the air, and their action on indicators loses thereby in sharpness. With barium hydroxide this is impossible, for the carbonate is insoluble, and is precipitated from the solution.

**Barium Nitrate**  $\text{Ba}(\text{NO}_3)_2$ . — This salt is made by the action of nitric acid on the sulphide, oxide, hydroxide, or carbonate of barium. It crystallizes from aqueous solution without water of hydration.

**Analytical Reactions of the Calcium Family.**—Barium-ion  $Ba^{++}$  is a colorless, bivalent ion. Many of its compounds are insoluble in water, and the sulphate is insoluble in acids also. The spectrum given by the salts contains a number of green and orange lines.

In solutions of salts of calcium, strontium, and barium, the ions may be distinguished by the fact that calcium sulphate solution will precipitate the strontium and barium as sulphates, but will leave salts of calcium unaffected. Similarly, strontium sulphate solution precipitates barium sulphate, and does not give any result with salts of the two first. The oxalate of calcium is precipitated in presence of acetic acid, while the oxalates of strontium and barium are not (*cf.* p. 714), and there are other differences of a like nature in the solubilities of the salts.

**Exercises.**—1. Arrange the chromates of the metals of this family in the order of solubility (see Table). Compare the solubilities with those of the carbonates, oxalates, and sulphates of the metals of the same family.

2. What must be the approximate total molar concentration of the solution of calcium chloride freezing at  $-48^{\circ}$  (p. 335)?

3. What is meant by fluorescence (*cf.* any book on physics)?

4. What will be the ratio by volume, at  $150^{\circ}$ , of the nitrogen peroxide and oxygen given off by the decomposition of calcium nitrate? What would be the nature of the difference between the ratio at  $150^{\circ}$  and that at room temperature?

5. What fact about the heat of solution of gypsum is indicated by its change of solubility with temperature (p. 717)?

6. What is the significance of the fact that hydrated barium chloride gives no hydrogen chloride when heated?

7. What are the advantages of removing water of hydration *in vacuo* (p. 731)?

8. Explain in terms of the ionic hypothesis the precipitation of the sulphate of strontium by calcium sulphate solution, and the absence of precipitation when the latter is added to the solution of a soluble salt of calcium.

9. Construct a table for the purpose of comparing the properties of the free elements of this family and also the properties of their corresponding compounds.

10. Are the elements of this family typical metals? If not, in what respects do they fall short (p. 645)?

11. Apply the rule of precipitation to the case of adding sodium carbonate to a solution of barium chloride.

12. What inference do you draw from the fact that the oxalates of barium and strontium are not precipitated in presence of acetic acid, while the oxalate of calcium is so precipitated? Is the inference confirmed by reference to the solubility data?

13. Explain the fact that strontium and calcium chromates are easily dissolved by acetic acid, while barium chromate is dissolved only by active mineral acids.

14. Explain the fact that all the carbonates, save those of sodium, potassium, and thallium, are precipitated in neutral solutions, but not in acidified solutions. Why is the precipitation incomplete when carbon dioxide is led through solutions of salts of the metals, but more complete when the hydroxides of the metals are used?

## CHAPTER XXXVI

### COPPER, SILVER, GOLD

THE three metals of this family, being found free in nature, are amongst those which were known in early times. They are the metals universally used for coinage and for ornamental purposes. They are the three best conductors of electricity (p. 645), and each represents the maximum of conductivity in the periodic series to which it belongs. In malleability and ductility silver is intermediate between gold and copper (p. 643), but in electrical conductivity it excels both.

**The Chemical Relations of the Copper Family.** — Copper (Cu, at. wt. 63.57), silver (Ag, at. wt. 107.88), and gold (Au, at. wt. 197.2), occupy the right side in the second column of the table of the periodic system (opposite inside of rear cover), and the chemical relations (p. 226) of these elements are in many ways in sharp contrast to those of the alkali metals, their neighbors, on the left side:

#### ALKALI METALS

Very active; rapidly oxidized by air; displace all other metals from combination (E. M. series, p. 404).

All univalent and give but one series of compounds. Halides all soluble in water.

Oxides and hydroxides strongly basic, and halides not hydrolyzed (p. 648).

Never found in anion. Give no complex cations.

#### COPPER, SILVER, GOLD

Amongst least active metals; only copper is oxidized by air; displaced by most other metals. Hence, found free in nature (p. 404).

$\text{Cu}^I$  and  $\text{Cu}^{II}$ : two series.  $\text{Ag}^I$ : one series.  $\text{Au}^I$  and  $\text{Au}^{III}$ : two series. Halides of univalent series insoluble.

Oxides and hydroxides feebly basic (except  $\text{Ag}_2\text{O}$ ); halides hydrolyzed (except Ag-halides). Hence, basic salts are numerous.

Frequently in anion, e.g.,  $\text{K.Cu(CN)}_2$ ,  $\text{K.Ag(CN)}_2$ ,  $\text{K.AuO}_2$ ,  $\text{K.Au(CN)}_2$ , and in complex cation, e.g.,  $\text{Ag(NH}_3)_2\text{OH}$  and  $\text{Cu(NH}_3)_4(\text{OH})_2$ .

On account of their inactivity towards oxygen, and their easy recovery from combination by means of heat, silver and gold, together with the platinum family, are known as the "noble metals."

Univalent copper and gold resemble in some ways  $\text{Hg}^{\text{I}}$  and  $\text{Tl}^{\text{I}}$ , while bivalent copper resembles  $\text{Zn}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Fe}^{\text{II}}$ , and  $\text{Ni}^{\text{II}}$ , and trivalent gold resembles  $\text{Pt}^{\text{IV}}$ . This family is, in fact, not homogeneous, and the close relation which, amongst metals, subsists between valence and chemical properties makes comparisons with elements of entirely different families often the most suggestive.

### COPPER Cu

**Chemical Relations of the Element.** — Copper is the first metallic element showing two valences which we have encountered. In such cases two more or less complete, independent series of salts are known. These are here distinguished as cuprous (univalent) and cupric (bivalent) salts. The methods by which a compound of one series may be converted into the corresponding compound of the other series should be noted.

The chief cuprous compounds are  $\text{Cu}_2\text{O}$ ,  $\text{CuCl}$ ,  $\text{CuBr}$ ,  $\text{CuI}$ ,  $\text{CuCN}$ ,  $\text{Cu}_2\text{S}$ . The cuprous compound is in each case more stable (p. 148) than the corresponding cupric compound, and is formed from it either by spontaneous decomposition, as in the cases of the iodide and cyanide ( $2\text{CuI}_2 \rightarrow 2\text{CuI} + \text{I}_2$ ), or on heating. The cuprous halides and cyanide are colorless and insoluble in water. Cuprous-ion  $\text{Cu}^+$  seems to be colorless. The cuprous salts of the oxygen acids are unstable.

The familiar cupric compounds are more numerous, as they include also stable salts of oxygen acids, like  $\text{CuSO}_4$ ,  $\text{Cu}(\text{NO}_3)_2$ , etc.  $\text{CuI}_2$  and  $\text{Cu}(\text{CN})_2$  cannot be obtained in pure form, as they decompose, giving the cuprous salts. The anhydrous salts are usually colorless or yellow, but cupric ion  $\text{Cu}^{++}$  is blue, and so, therefore, are the aqueous solutions of the salts. The cupric are more familiar than the cuprous compounds, since cupric oxide, sulphate, and acetate are the compounds of copper which most frequently find employment in chemistry and in the arts. All the soluble salts of copper are poisonous.

In electrolyzing salts of copper, a given amount of electricity will deposit twice as much copper from a cuprous salt as from a cupric salt (p. 350), since cuprous-ion carries only half as great a charge, weight for weight, as cupric-ion.

Writers on chemistry still (p. 137) frequently double ( $\text{Cu}_2\text{Cl}_2$ , etc.) the formulæ of cuprous salts. The molecular weights in organic solvents (cf. p. 335), however, in many cases accord with the simple

formulae. Some higher molecular weights observed in solution and the vapor density of cuprous chloride (6.6, corresponding nearly to  $\text{Cu}_2\text{Cl}_2$ ) might be regarded as being due to association (imperfect dissociation, cf. p. 282). The formation of numerous double or complex compounds like  $\text{HCl}, \text{CuCl}$  ( $=\text{HCuCl}_2$ ), which may be regarded as acid salts, however, lends support to the view that the formulae should be doubled. Inasmuch as the behavior of the salts is sufficiently well represented by the simple formulae, these are here used throughout (see under Silver, p. 749).

In addition to (1) **having two valences**  $\text{Cu}^I$  and  $\text{Cu}^{II}$ , and therefore two series of compounds (*two oxides, two chlorides, etc.*), *each* of these states of copper also joins with other elements to form (2) **complex positive ions** such as  $\text{Cu}(\text{NH}_3)_2^+$  and  $\text{Cu}(\text{NH}_3)_4^{++}$ , just as hydrogen and nitrogen form the complex positive ion  $\text{NH}_4^+$ , and the univalent form also gives (3) **stable complex negative ions** such as  $\text{Cu}(\text{CN})_2^-$ ,  $\text{CuCl}_2^-$ . None of the metallic elements discussed in the two preceding chapters showed any of these peculiarities. Many of the metals to be discussed later exhibit one or more of them, however. **Especial attention should therefore be given to the chemistry of copper**, in order that the behavior which such relations entail may be mastered at the first encounter, and the same relations may be instantly recognized and understood when they reappear in other connections.

There is only one other peculiarity which a metallic element frequently shows, although copper does *not* exhibit it. This is (4) **the ability of its hydroxide to be, not only basic, as metallic hydroxides by definition (p. 646) must be, but also acidic**. This behavior we encounter first in the case of gold (see p. 760) and in simpler and more familiar form in the case of zinc (see next chapter).

**Occurrence.** — Copper is found free in the Lake Superior region, in China, and in Japan. The sulphides, copper pyrites  $\text{CuFeS}_2$  and chalcocite  $\text{Cu}_2\text{S}$ , are worked in Montana, in southwest England, and in Spain. Malachite,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  ( $=\text{Cu}(\text{OH})_2, \text{CuCO}_3$ ), and azurite,  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$  ( $=\text{Cu}(\text{OH})_2, 2\text{CuCO}_3$ ), both basic carbonates, are mined in Arizona, Siberia, and elsewhere. Cuprite or ruby copper  $\text{Cu}_2\text{O}$  is also an important ore. The name of the element comes from the fact that in ancient times copper mines, long since worked out, existed in Cyprus. The element is found in the feathers of some birds, in the hæmocyanin of the blood of the cuttle-fish.

which is blue when arterial and colorless when venous, and elsewhere in living organisms.

**Extraction from Ores.** — For isolating native copper it is only necessary to separate the metal, by grinding and washing, from the rock through which it ramifies, and to melt the almost pure powder of copper with a flux (p. 652). The carbonate and oxide ores require coal, in addition, for the removal of the oxygen.

The liberation of copper from the sulphide ores is difficult, and often involves very elaborate schemes of treatment. This arises from the fact that many copper ores contain a large amount of the sulphides of iron, and these have to be removed by conversion into oxide (by roasting) and then into silicate (with sand). The silicate forms a flux, and separates itself from the molten copper sulphide ("matte"). In Montana it is found possible to abbreviate the treatment. The ore is first roasted until partially oxidized. It is then melted in a cupola or a reverberating furnace, and placed in large iron vessels like Bessemer converters (*q.v.*) provided with a lining rich in silica. A blast of air mixed with sand is now blown through the mass. The iron is completely oxidized to  $\text{FeO}$  and made into silicate  $\text{FeSiO}_3$ , the sulphur escapes as sulphur dioxide, and arsenic and lead are likewise removed by this treatment. The silicate of iron floats as a slag upon the copper when the contents of the converter are poured out. The resulting copper is pure enough to be cast in large plates and purified by electrolysis (see p. 747).

Much copper ore is of low grade, containing perhaps only 2 per cent of copper ore and 98 per cent of rock material. From such ores the usual methods of washing often recover only 70 per cent or less of the copper ore present, and 30 per cent or more is lost. The **froth flotation process** raises the proportion recovered to 85 or 90 per cent of the whole. The finely crushed ore is agitated with water, to which is added some cheap oil and sometimes a little sulphuric acid. The mixture is then allowed to flow into a larger tank of water, in which the rock material immediately sinks to the bottom while the particles of ore are contained in the oily froth which rises to the top. The plant also occupies less than one-tenth of the space, and uses less than half the power required for treating the same amount of ore by washing.

The world's production (1913) is about a million metric tons, of which the United States furnished 58 per cent, South America 11, Japan 6, and Germany 4. The proportions of the whole consumed



were, approximately, United States 33 per cent, Great Britain 22 per cent, Germany 22 per cent.

**Physical Properties.** — Copper is red by reflected and greenish by transmitted light. Native copper shows crystals of the regular system (p. 172). It melts at  $1083^{\circ}$ , and therefore much more easily than pure iron ( $1530^{\circ}$ ). Its density is 8.93. When steel draw-plates are used, it can be drawn into wire with a diameter of only 0.2 mm., and by means of plates provided with perforated diamonds the diameter of the wire can be reduced to 0.03 mm. (1 kilometer weighs only 7 g.). The metal after drawing is more tenacious, but conducts electricity less well. Copper has a transition point at  $71.7^{\circ}$ , and shows different physical properties above that point.

**Chemical Properties.** — In dry oxygen, copper does not rust. In moist oxygen a thin film of cuprous oxide is formed, and in ordinary air a green basic carbonate (*not* verdigris, *q.v.*). It does not decompose water at any temperature or displace hydrogen from dilute acids (p. 404). On the other hand, hydrogen, absorbed in platinum or even in charcoal, liberates copper:  $\text{Cu}^{++} + \text{H}_2 \rightarrow \text{Cu} + 2\text{H}^{+}$ , when immersed in solutions of copper salts. The metal attacks oxygen acids (pp. 425, 535), however. Again, acids like hydrochloric acid, in conjunction with oxygen from the air, do act slowly upon copper:  $2\text{Cu} + 4\text{HCl} + \text{O}_2 \rightarrow 2\text{CuCl}_2 + 2\text{H}_2\text{O}$ . This sort of simultaneous action of two agents is frequently used, as in making silicon tetrachloride (p. 632). In a similar way sea-water and air slowly corrode the copper sheathings of ships, giving a basic chloride,  $\text{Cu}_4(\text{OH})_6\text{Cl}_2 \cdot \text{H}_2\text{O}$  ( $= 3\text{Cu}(\text{OH})_2 \cdot \text{CuCl}_2 \cdot \text{H}_2\text{O}$ ), which is found in nature as atacamite.

On account of its resistance to the action of acids, copper is used for many kinds of vessels, for covering roofs and ships' bottoms, and for coins. It furnishes also electrotype reproductions of medals, of engraved plates, of type, etc. (see p. 746). In the mines near Butte, the presence of sulphuric acid in the water, which attacks steel, compels the use of pumping machinery of copper.

**Alloys.** — The qualities of copper are modified for special purposes by alloying it with other metals. Brass contains 18–40 per cent of zinc, and melts at a lower temperature (p. 644) than does copper. A variety with little zinc is beaten into thin sheets, giving Dutch-metal ("gold-leaf"). Bronze contains 3–8 per cent of tin, 11 or more per cent of zinc, and some lead. It was used for making

weapons and tools before means of hardening iron were known, and later, on account of its fusibility, continued to be employed for castings until displaced largely by cast-iron (discovered in the eighteenth century). For works of art it is preferred to copper because of its fusibility, its color, and its more rapid acquirement of a much prized "patina," due to surface corrosion. Artificial "bronzing" of brass is affected by applying a solution of arsenious oxide in hydrochloric acid ( $\text{AsCl}_3$ ). The zinc displaces some arsenic, which combines with the copper. Brass instruments are "bronzed" by means of a dilute solution of chloroplatinic acid (*q.v.*), from which the zinc displaces platinum. **Gun-metal** contains 10 per cent, and **bell-metal** 20–24 per cent of tin. **German silver** contains 19–44 per cent of zinc and 6–22 per cent of nickel, and shows none of the color of copper. **Aluminium-bronze** contains 5–10 per cent of aluminium, and resembles gold in color. When it contains some iron, it can be worked at a red heat, but not welded. **Silicon-bronze** contains not more than 5 per cent of silicon, and is made by adding silicide of copper (made in the electric furnace, p. 569) to copper. It has usually only 60 per cent of the conductivity of pure copper, but is nearly twice as tenacious, and is used for telephone and over-head electric wires. **Phosphor-bronze** contains copper and tin (100 : 9) with  $\frac{1}{4}$ –1 part of phosphorus, and is employed for certain parts of machines. Ships' propellers are made of **manganese-bronze** (30 per cent manganese). In many of these alloys the metals are partly in the form of chemical compounds, such as  $\text{Cu}_3\text{Sn}$  and  $\text{Cu}_2\text{Zn}_3$ .

**Cupric Chloride  $\text{CuCl}_2$ .**— This compound is made by union of copper and chlorine, by treating the hydrate or carbonate with hydrochloric acid, or by heating copper with hydrochloric acid and some nitric acid, the latter being used simply as an oxidizing agent:  $\text{Cu} + 2\text{HCl} + \text{O} \rightarrow \text{CuCl}_2 + \text{H}_2\text{O}$ . The blue crystals of a **hydrate**,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , are deposited by the solution. The **anhydrous salt** is yellow. Dilute solutions are blue, the color of cupric-ion, but concentrated solutions are green on account of the presence of the yellow molecules (p. 378). The aqueous solution is acid in reaction (p. 399). When excess of ammonium hydroxide is added to the solution, the basic chloride, **cupric oxychloride**  $\text{Cu}_4(\text{OH})_6\text{Cl}_2$  (p. 738), which is at first precipitated, redissolves, and a deep-blue solution is obtained. This on evaporation yields deep-blue crystals of hydrated **ammonio-cupric chloride**  $\text{Cu}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ . The deep-blue color of the solution, which is given by all cupric salts, is that of ammonio-

cupric-ion  $\text{Cu}(\text{NH}_3)_4^{++}$ . The dry salt also absorbs ammonia, giving  $\text{CuCl}_2 \cdot 6\text{NH}_3$ . This and the preceding compound have an appreciable tension of ammonia, and when warmed, or placed under reduced pressure, leave first  $\text{CuCl}_2 \cdot 2\text{NH}_3$ , and finally  $\text{CuCl}_2$ .

**Cuprous Chloride  $\text{CuCl}$ .** — This salt is formed when dry cupric chloride is heated:  $2\text{CuCl}_2 \rightleftharpoons 2\text{CuCl} + \text{Cl}_2$ . It may be made by boiling cupric chloride solution with hydrochloric acid and copper turnings:



The solution contains compounds of cuprous chloride with hydrogen chloride  $\text{HCl} \cdot \text{CuCl}$  or  $\text{HCuCl}_2$  and  $\text{H}_2\text{CuCl}_3$ , which are decomposed when water is added. The cuprous chloride is insoluble in water, and forms a white crystalline precipitate.

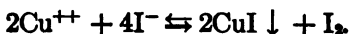
Cuprous chloride is hydrolyzed quickly by hot water, giving, finally, red, hydrated cuprous oxide,  $\text{Cu}_2\text{O}$ . When dry it is not affected by light, but in the moist state becomes violet and, finally, nearly black. The action is said to be  $2\text{CuCl} \rightarrow \text{CuCl}_2 + \text{Cu}$ , the copper being adsorbed as a colloid (hence the color changes). In moist air it turns green, and is oxidized to cupric oxychloride (p. 739). It is dissolved by hydrochloric acid, giving the colorless complex acids  $\text{HCuCl}_2$  and  $\text{H}_2\text{CuCl}_3$ . The solution is oxidized by the air, turning first brown and then green. Cuprous chloride also dissolves in ammonium hydroxide, giving ammonio-cuprous chloride, probably  $\text{Cu}(\text{NH}_3)_2\text{Cl}$ , the ion  $\text{Cu}(\text{NH}_3)_2^+$  being colorless. The solution is quickly oxidized by the air, turns deep-blue, and then contains  $\text{Cu}(\text{NH}_3)_4^{++}$ . The solution of cuprous chloride in hydrochloric acid is used for absorbing carbon monoxide from gaseous mixtures. A crystalline compound ( $\text{CuCO} \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$  ?) has been isolated from the solution.

**The Bromides and Iodide of Copper.** — By treatment of copper with bromine-water, and slow evaporation of the solution, jet-black crystals of anhydrous cupric bromide  $\text{CuBr}_2$  are obtained. A concentrated aqueous solution is deep-brown in color, and the gradual ionization of the molecules as the solution is diluted is well shown by this salt (p. 378). The ionization is here accompanied by evolution of heat (p. 368), as it is also in the cases of cupric chloride and cupric sulphate, and in the ionized condition the substances contain less available energy than in the molecular. In these cases, there-

fore, when the temperature is raised the ionization diminishes (p. 305).

When cupric bromide is heated, bromine is given off, and cuprous bromide  $\text{CuBr}$  remains.

Cupric iodide  $\text{CuI}_2$  appears to be unstable at ordinary temperatures. When a soluble iodide is added to a cupric salt, a white precipitate of cuprous iodide  $\text{CuI}$  and free iodine are obtained:



The iodine may be dissolved in excess of a soluble iodide (p. 665), or reduced to hydrogen iodide with sulphurous acid (p. 445).

**The Solution of Insoluble Salts when Complex Ions are Formed.** — The solution of an insoluble salt like cuprous chloride by hydrochloric acid or ammonium hydroxide is typical of a great variety of actions of which we here meet one of the first examples (cf. p. 405). The explanation involves only principles already used in other cases.

Since a salt is normally less soluble in an acid having the same anion (p. 699), the dissolving of cuprous chloride in hydrochloric acid requires a special explanation, namely, the fact that here a soluble complex acid,  $\text{H.CuCl}_2$  is formed. The chloride-ion of the hydrogen chloride must indeed tend to repress the ionization of the dissolved part of the cuprous chloride, so that a smaller concentration of  $\text{Cu}^+$  remains. But the complex negative ion  $\text{CuCl}_2^-$  which is formed, is very little dissociated, and gives a still smaller concentration of  $\text{Cu}^+$  ( $\text{CuCl}_2^- \rightleftharpoons \text{Cu}^+ + 2\text{Cl}^-$ ). The ion-product of cuprous chloride, and the concentration relations of the ionic substance  $\text{CuCl}_2^-$  and its dissociation products ( $\text{Cu}^+$  and  $2\text{Cl}^-$ ) are symbolized as follows:

$$[\text{Cu}^+] \times [\text{Cl}^-] = K' \qquad \frac{[\text{Cu}^+] \times [\text{Cl}^-]^2}{[\text{CuCl}_2^-]} = K.$$

The value of  $[\text{Cu}^+]$  from cuprous chloride (first formula) is, in general, *greater* than its value from the ion  $\text{CuCl}_2^-$  of  $\text{H.CuCl}_2$  (second formula), when excess of  $\text{HCl}$  is present. Hence, the  $\text{Cu}^+$  tends to pass over into the more stable compound, where it is more completely combined. More  $\text{CuCl}$  dissolves to replace the  $\text{Cu}^+$  which has been removed, and the change stops when the  $\text{CuCl}$  is all dissolved, or the values of  $[\text{Cu}^+]$  from both compounds have become equal. Thus, the complex ion is formed at the expense of



**Cuprous Oxide  $\text{Cu}_2\text{O}$ .** — This oxide is red in color, and natural specimens show octahedral forms. It is produced by oxidation of finely divided copper at a gentle heat, or by the addition of bases to cuprous chloride, and is best made by the action of glucose (p. 605) on cupric hydroxide (see Fehling's solution, below). The latter is reduced by the former, and the resulting hydrated cuprous oxide forms a pale-brown precipitate which quickly becomes bright red. The simple hydroxide  $\text{CuOH}$  is unknown, but the above mentioned precipitate has approximately the composition  $4\text{Cu}_2\text{O} \cdot \text{H}_2\text{O}$ , and yields  $\text{Cu}_2\text{O}$  when heated.

Cuprous oxide is acted upon by hydrochloric acid, giving cuprous chloride, or rather  $\text{HCuCl}_2$ . It also dissolves in ammonium hydroxide, giving, probably,  $\text{Cu}(\text{NH}_3)_2\text{OH}$ , which is colorless. With dilute oxygen acids part of it is oxidized, giving the cupric salt, and part is reduced to metallic copper:



**Cupric Oxide and Hydroxide.** — Cupric oxide  $\text{CuO}$  (black) is formed by heating copper in a stream of oxygen, or by igniting the nitrate, carbonate, or hydroxide. Although not soluble in water, it absorbs moisture from the air, probably because it is porous and has much surface. When heated strongly it loses some oxygen, and is partly reduced to cuprous oxide. Its chief use is in the analysis of compounds of carbon. When heated with the latter it oxidizes the hydrogen to water, and the carbon to carbon dioxide. The operation is performed in a tube through which passes a stream of oxygen, and the products are caught in glass vessels containing calcium chloride and potassium hydroxide, respectively, and the increase in weight of each is determined.

**Cupric hydroxide**  $\text{Cu}(\text{OH})_2$  is precipitated as a gelatinous substance by addition of sodium or potassium hydroxide to a solution of a cupric salt:  $\text{Cu}^{++} + 2\text{OH}^- \rightarrow \text{Cu}(\text{OH})_2$ . When the mixture is boiled, the hydroxide loses water and forms a black, hydrated cupric oxide  $\text{Cu}(\text{OH})_2 \cdot 2\text{CuO}$  (?).

The hydroxide interacts with ammonium hydroxide, forming the soluble compound  $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$ , which imparts a deep-blue color to the solution. Various forms of cellulose, such as filter paper and cotton, dissolve in this solution and are reprecipitated when the ammonium hydroxide is neutralized with sulphuric acid. **Artificial silk** is made by pressing the solution through dies into the precipitant. Paper and cotton goods, when passed first through one

and then the other of these liquids, receives a tough, waterproof surface.

Cupric hydroxide interacts with a solution of sodium tartrate  $\text{Na}_2(\text{CO}_3)_2\text{C}_2\text{H}_2(\text{OH})_2$ , giving a deep-blue liquid (practically "Fehling's solution"). In this action, it enters into the negative ion, as is shown by electrolysis, interacting apparently with the hydroxyl groups of the tartrate-ion. The solution is used in testing for, and estimating quantities of glucose (p. 605), and other reducing substances. Cuprous oxide is precipitated (see p. 743).

**Cupric Nitrate  $\text{Cu}(\text{NO}_3)_2$ .** — The nitrate is made by treating cupric oxide or copper with nitric acid (p. 535), and is obtained from the solution as a deliquescent, crystalline hydrate. The **hexahydrate** is secured at temperatures below  $24.5^\circ$ , its transition point (p. 689), and the **trihydrate** from  $24.5^\circ$  up to  $114.5^\circ$  (its transition point; see under Manganous sulphate). When dehydrated at  $65^\circ$  the salt is partly hydrolyzed, and a basic nitrate  $\text{Cu}_4(\text{OH})_6(\text{NO}_3)_2$  remains.

**Carbonate of Copper.** — No normal carbonate  $\text{CuCO}_3$  can be obtained. A **basic carbonate** (malachite) is found in nature, and is precipitated by adding soluble carbonates to cupric salts:



The carbonate, if formed, would be hydrolyzed by water (p. 647).

**Cyanides of Copper.** — With potassium cyanide and a solution of a cupric salt, **cupric cyanide**  $\text{Cu}(\text{NC})_2$  is precipitated. This is not stable, however, and gives off cyanogen, leaving **cuprous cyanide**:



Cuprous cyanide is insoluble in water, but interacts with an excess of potassium cyanide solution, producing a colorless liquid, from which  $\text{K.Cu}(\text{CN})_2$  ( $=\text{KCN.CuCN}$ ) **potassium cuprocyanide**, may be obtained in colorless crystals. The complex anion  $\text{Cu}(\text{CN})_2^-$  is so little ionized to  $\text{Cu}^+$  and  $2\text{CN}^-$  that all insoluble copper compounds, *including cupric sulphide*, interact with potassium cyanide; and none of them can be precipitated from the solution. Zinc is actually unable to displace copper from such a solution. The cause of the solution of the salts is the same as when the complex ions  $\text{Cu}(\text{NH}_3)_2^+$ ,  $\text{Cu}(\text{NH}_3)_4^{++}$ , and  $\text{CuCl}_2^-$  are formed (p. 741).

**Cupric Acetate.**— By the oxidation of plates of copper, separated by cloths saturated with acetic acid (vinegar), a basic acetate of copper (**verdigris**) is obtained:



It is used in manufacturing green paint, is insoluble in water, and is unaffected by light. It dissolves in acetic acid, and green crystals of the **normal acetate**  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$  are obtained from the solution. The basic acetate is used in preparing **Paris green**. A hot solution of arsenious acid  $\text{H}_3\text{AsO}_3$  is mixed with a paste of verdigris and a little acetic acid and boiled. A precipitate of Paris green  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Cu}_3(\text{AsO}_3)_2$ , which has a unique light-green color, is thrown down. On account of their poisonous nature, this compound and **Scheele's green**  $\text{CuHAsO}_3$  are little used as pigments. The former is chiefly made for use in the extermination of potato-beetles and other insects and for employment in the destruction of parasitic fungi.

**Cupric Sulphate**  $\text{CuSO}_4$ .— This salt is obtained by heating copper in a furnace with sulphur, and admitting air to oxidize the cuprous sulphide. The mixture of cupric sulphate and cupric oxide which is formed is treated with sulphuric acid. The salt is also made by allowing dilute sulphuric acid to trickle over granulated copper while air has free access to the material:  $2\text{Cu} + 2\text{H}_2\text{SO}_4 + \text{O}_2 \rightarrow 2\text{CuSO}_4 + 2\text{H}_2\text{O}$ . When concentrated and at a high temperature, sulphuric acid will itself act as the oxidizing agent (*cf.* p. 425).

Cupric sulphate crystallizes as **pentahydrate**  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in blue asymmetric crystals (Fig. 55, p. 151), and in this form is called **blue-stone** or **blue vitriol**. The dissociation of this hydrate has been discussed on page 153. The aqueous solution has an acid reaction (p. 399). The anhydrous salt is white, and can be crystallized in thin needles (rhombic system?) from solution in hot, concentrated sulphuric acid (*cf.* pp. 151–154). Cupric sulphate is employed in copper-plating (see p. 747), in batteries, and as a mordant in dyeing (*q.v.*). A minute proportion is added to drinking water, to destroy *algæ*, which otherwise propagate in the reservoirs and give a disagreeable taste and odor to the water. The seeds of cereals are moistened with a dilute solution, before planting, to prevent the growth of fungi (*smuts*). A solution, mixed with milk of lime ( $\text{Cu}(\text{OH})_2$  is precipitated), **Bordeaux mixture**, is largely used as a spray on grape vines and other plants to prevent the growth of fungi.



When ammonium hydroxide is added to cupric sulphate solution, a pale-green basic sulphate  $\text{Cu}_4(\text{OH})_6\text{SO}_4(?)$  is first precipitated. With excess of the hydroxide, the blue  $\text{Cu}(\text{NH}_3)_4^{++}$  ion (p. 742) is formed, and crystals of **ammonio-cupric sulphate**  $\text{Cu}(\text{NH}_3)_4.\text{SO}_4.\text{H}_2\text{O}$  can be obtained from the solution. This compound easily loses water and ammonia (by stages), leaving successively  $\text{CuSO}_4.2\text{NH}_3$  and  $\text{CuSO}_4.\text{NH}_3$ . Cupric sulphate also combines with potassium and ammonium sulphates, giving double salts of the form  $\text{CuSO}_4.\text{K}_2\text{SO}_4.6\text{H}_2\text{O}$ , which are deposited in large, monosymmetric crystals from the mixed solutions (see Zinc sulphate).

**The Sulphides of Copper.** — **Cuprous sulphide**  $\text{Cu}_2\text{S}$  occurs in nature in rhombic crystals of a gray, metallic appearance. It is the sulphide formed by direct union of the elements.

**Cupric sulphide**  $\text{CuS}$  is deposited as a black precipitate when hydrogen sulphide is led through a solution of a cupric salt. By cautiously treating copper with excess of sulphur at  $114^\circ$  it may be obtained as a blue crystalline solid. At higher temperatures it gives off sulphur.

**Analytical Reactions of Compounds of Copper.** — The ion of ordinary cupric salts, cupric-ion  $\text{Cu}^{++}$ , is blue, and that of cuprous salts, cuprous-ion  $\text{Cu}^+$ , is colorless. Cuprous solutions, however, are easily oxidized by the air and become blue. In solutions containing cupric-ion, hydrogen sulphide precipitates cupric sulphide, even in presence of acids (p. 421). Bases throw down the blue hydroxide, and carbonates precipitate a green basic salt (p. 744). Potassium ferrocyanide gives the brown, gelatinous cupric ferrocyanide:  $2\text{Cu}.\text{SO}_4 + \text{K}_4.\text{Fe}(\text{CN})_6 \rightleftharpoons \text{Cu}_2.\text{Fe}(\text{CN})_6 \downarrow + 2\text{K}_2\text{SO}_4$ . A very characteristic test is the formation of the deep-blue  $\text{Cu}(\text{NH}_3)_4^{++}$  ion with excess of ammonium hydroxide. This solution, because of the very slight concentration of  $\text{Cu}^{++}$ , gives a precipitate with hydrogen sulphide only. Solutions of complex cuprous cyanides such as potassium cuprocyanide  $\text{K}.\text{Cu}(\text{CN})_2$  are colorless, and do not respond to any of the above tests. With microcosmic salt or borax (pp. 560, 640), copper compounds form a bead which is green in the oxidizing part of the flame and becomes red and opaque (liberation of copper) in the reducing flame.

**Electrotyping.** — When plates of platinum, connected with a battery, are immersed in cupric sulphate solution, copper is deposited

on the cathode (negative pole). The sulphate-ion  $\text{SO}_4^{=}$  migrates (p. 347) towards the anode (positive pole) and there produces sulphuric acid and oxygen (p. 344). If, however, the anode is made of *copper*, the  $\text{SO}_4^{=}$  migrates, but is not discharged. Instead, copper goes into solution (Fig. 147) as  $\text{Cu}^{++}$ , in amount equal to that deposited on the other pole. Thus, the only changes are, (1) an increase in concentration of cupric sulphate round the positive pole (anode), and (2) a transfer of copper from the copper anode to the cathode (see below).

A copper **electrotype** of a medal (or a page of type) is made by first preparing a cast of the medal in plaster of Paris, gutta percha, or wax. The surface of the cast is then rubbed with graphite, to render it a conductor, and the cast is then used as the cathode in a cell with a copper anode, like that just described. The deposit of copper, when heavy enough, is stripped off. In making book plates, the cast is made with wax, and the copper electrotype is strengthened and thickened by filling the back with melted lead.\*

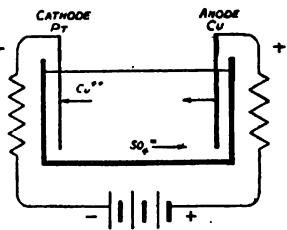


FIG. 147.

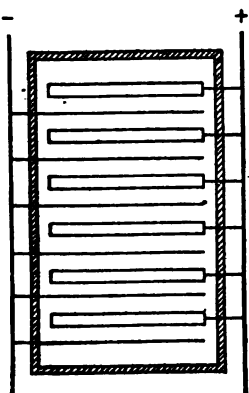


FIG. 148.

**Copper Refining.**—The tenacity, ductility, and conductivity of copper are seriously affected by small amounts of impurities, such as cuprous oxide or sulphide, which are soluble in the molten metal. Arsenic amounting to 0.03 per cent lowers the conductance about 14 per cent. There are also silver and gold in smelter copper. Hence, a large proportion of the copper on the market is purified by electrolysis. The principle is the same as that used in electrotyping. Thin sheets of copper form the cathodes, and thick plates

of crude copper the anodes. These are suspended alternately and close together in large troughs, lined with lead, and filled with cupric sulphate solution (Fig. 148, diagrammatic, view from above). The cathodes are all connected with the negative wire of the dynamo, and the anodes with the positive one. The  $\text{Cu}^{++}$  is attracted to the

\* For newspapers, a plate is made from the cast of the type more quickly by means of melted **stereotype metal** (lead, antimony, tin; 82 : 15 : 3).

cathodes and is deposited upon them. The  $\text{SO}_4^{=}$  migrates towards the anodes, where copper from the thick plate forms ions  $\text{Cu}^{++}$  in equivalent amount. The stock of cupric sulphate thus remains the same, and the liquid is stirred to keep the sulphate from accumulating close to the anodes. The practical effect of the electrolysis is to carry copper across from one plate to the other. The cathodes are removed from time to time, and the deposit of copper is stripped from their surface. Fresh anodes are substituted when the old ones are eaten away. Since there is no final decomposition of any cupric sulphate, the only electrical energy required is that necessary to overcome the friction of the moving ions. Hence, a very small difference in potential (less than 0.5 volts) is sufficient (see p. 799).

The less active metals, which are mixed with the copper in the anode, are not ionized, because there is plenty of the more active copper to carry the current. These metals, and traces of sulphides, therefore, fall to the bottom of the vat as a sludge. Zinc and other metals more active than copper, however, are ionized. Conversely, at the cathode, the copper, being the least active metal present in ionic form, is alone deposited. There is no tendency to discharge zinc or hydrogen, for example, so long as there are plenty of the more easily discharged copper ions available (see p. 799). In this way, copper, 99.8 per cent pure, is obtained, gold and silver are recovered from the sludge, and the bath liquid is removed from time to time for purification from the more active metals it acquires. In 1914, in the United States alone, 264,825 ounces of gold and nearly fifteen million ounces of silver were obtained in this way.

#### SILVER Ag

***Chemical Relations of the Element.*** — This element presents a curious assortment of chemical properties. It differs from copper in having a strongly basic oxide, in giving salts with active acids which are not hydrolyzed by water, and in forming neutral rather than basic salts. In these respects it approaches the metals of the alkalis and alkaline earths. It resembles copper in entering into complex compounds, and in giving insoluble halides like the cuprous halides. It differs from both copper and the metals of the alkalis, and resembles gold and platinum, in that its oxide is easily decomposed by heat, with formation of the free metal, and in the low position it occupies in the electromotive series and the consequent slight chemical activity of the free metal.

The salts are always represented by the simplest formula,  $\text{AgCl}$ , etc., although in organic solvents greater tendencies to polymerization are observed than in the case of the cuprous compounds (p. 735).

**Occurrence.** — Native silver, sometimes found in large masses, although more usually scattered through a rocky matrix, contains varying amounts of gold and copper. Native copper always contains dissolved silver. Sulphide of silver  $\text{Ag}_2\text{S}$  occurs alone and dissolved in galenite  $\text{PbS}$ , with which it is isomorphous. Smaller amounts of the metal are obtained from pyrargyrite  $\text{Ag}_3\text{SbS}_3$  and proustite  $\text{Ag}_3\text{AsS}_3$ , which are silver sulphantimonite and sulpharsenite, respectively, and from horn-silver  $\text{AgCl}$ . The chief supplies come from California, Australia, and Mexico.

**Metallurgy.** — The silver contained free, or as sulphide, in ores of copper and lead, is found in the free state dissolved in the metals extracted from these ores, and is secured by refining them. In the electrolytic refining of copper, silver is obtained from the sludge deposited in the baths (p. 747). The proportion present in lead is usually small. Formerly the **Pattinson desilverizing process** was largely employed. In it the metallic lead is melted in iron vessels, and the crystals of lead, deposited as the metal slowly loses heat, are raked out. These consist at first of pure lead (cf. p. 199). When the remaining liquid becomes saturated with silver it begins to deposit lead and silver together. At this point the residue is placed in a hollow, lined with bone-ash, forming part of a reverberatory furnace (Fig. 143, p. 686), and heated strongly while a blast of air passes over its surface. In this process, called "cupellation," the lead is converted into litharge  $\text{PbO}$ , which, driven by the air, flows in molten condition over the edge of the cupel. When the last trace of lead is gone, the shining surface of the pure silver "flashes" into view (cf. p. 659). **Parke's process**, which has superseded the above, takes advantage of the fact that molten zinc and lead are practically insoluble in one another, while silver is much more soluble in zinc than in lead. Lead dissolves 1.6 per cent of zinc, and zinc 1.2 per cent of lead. The principle is the same as in the removal of iodine from water by ether (p. 275). The lead is melted and thoroughly mixed by machinery with a small proportion of zinc. After a short time the zinc floats to the top, carrying with it in solution almost all of the silver, and solidifies at a temperature at which the lead is still molten. The zinc-silver alloy, largely a com-

pound  $\text{Ag}_3\text{Zn}_2$ , is skimmed off, and heated moderately in a furnace to permit the adhering lead to drain away. The zinc is finally distilled off in clay retorts, and the lead remaining with the silver is removed by cupellation.

The gold which goes with the silver in Parke's process is separated electrolytically (p. 747). Plates of the silver-gold alloy form the anode, and silver nitrate solution the vat-liquid. The silver, being the more active metal, is ionized and deposited on the cathode, while the gold collects as a powder in a bag surrounding the anode.

Ores of silver which do not contain much or any lead are often smelted with lead ores, and the product is treated as described above, but many other processes are in use. In Mexico the "patio" process has been in use since 1557. The sulphide is converted into chloride by the action of cupric chloride. Metallic mercury displaces the silver:  $\text{AgCl} + \text{Hg} \rightarrow \text{HgCl} + \text{Ag}$ , and, being present in excess, dissolves it. The treatment occupies several weeks, and much mercury is consumed. The amalgam is finally secured by "washing," and the mercury is separated from the silver by distillation.

During the first half of the nineteenth century the total world's output averaged only 643 tons per year. Up to 1870 a gram of gold could buy 15.5 g. of silver. Now that the production has reached about 8000 tons, the same amount of gold purchases about 40 g. The chief sources (1911) are Mexico 2460 tons, United States 1890, Canada 1018, Europe 525.

**Physical Properties.**—Pure silver is almost perfectly white. It melts at  $960^\circ$ . Its density is 10.5. Its ductility is so great that wires can be drawn of such fineness that 2 kilometers weigh only about 1 g. In the molten condition it absorbs mechanically about twenty-two times its own volume of oxygen, but gives up almost all of this as it solidifies. Fantastically irregular masses result from the "sprouting" or "spitting" which accompanies the escape of the gas.

By addition of ferrous citrate to silver nitrate, a red solution and lilac precipitate of free silver can be made. The latter, after washing with ammonium nitrate solution, gives a red colloidal suspension (p. 621) in water. It is a negatively charged colloid, and is coagulated by bivalent positive ions. Colloidal (cf. p. 621) silver showing a variety of colors, due to different degrees of dispersion, has been prepared by Cary Lea. Colloidal suspensions of metals are formed

also by passing an electrical discharge between wires of silver, gold, or platinum held under water.

Silver is alloyed with copper to render it harder. The silver coinage of the United States and the continent of Europe has a "fineness of 900" (900 parts of silver in 1000), that of Great Britain 925. Silver ornaments have a fineness of 800 or more. A superficial layer of almost pure-white silver is produced by heating the object in the air and dissolving out the cupric oxide thus formed with dilute sulphuric acid. The surface of the products, if not subsequently burnished, is "frosted." "Oxidized silver" is made by dipping objects made of the metal in a solution of potassium-hydrogen sulphide, whereby a thin film of silver sulphide is produced.

**Chemical Properties.** — Silver, when *cold*, is oxidized by ozone, but not by oxygen (see silver oxide). It does not ordinarily displace hydrogen from aqueous solutions of acids, but its tendency to form the sulphide is so great that it decomposes hydrogen sulphide and alkali sulphides (*cf.* p. 441). Hence, sulphur compounds in the air tarnish the surface, producing  $\text{Ag}_2\text{S}$ , as do also eggs, secretions from the skin (proteins, p. 628), and vulcanized rubber. It also displaces hydrogen when boiled with concentrated hydriodic acid, giving  $\text{AgHI}_2$  (*cf. Aqua regia*, p. 537). Silver interacts with cold nitric acid and with hot, concentrated sulphuric acid, giving the nitrate or sulphate of silver and oxides of nitrogen or of sulphur (p. 535). Since its hydroxide has no tendency to behave as an acid, alkalies, whether in solution or fused, have no action upon silver. Hence alkaline substances are heated in vessels of this metal or of iron, rather than in vessels of platinum (*q.v.*), because platinum is attacked by alkaline materials.

**The Halides of Silver.** — The **chloride**  $\text{AgCl}$ , **bromide**  $\text{AgBr}$ , and **iodide**  $\text{AgI}$  are formed as curdy precipitates when a salt of silver is added to a solution containing the appropriate halide ion. The first is white, and melts at about  $457^\circ$ . The second and third are very pale-yellow and yellow respectively. The insolubility in water, which is very great, increases in the above order. The iodide, after melting, solidifies and forms quadratic crystals, which, as they cool, pass at  $146^\circ$  (transition point) into a different physical variety (hexagonal) with evolution of heat (*cf.* pp. 679, 738).

When exposed to light, the chloride becomes first violet (colloidal silver, dispersed in the  $\text{AgCl}$ ) and finally brown, chlorine being

liberated. The bromide and iodide behave similarly. Solid silver chloride absorbs ammonia, forming with a low pressure  $2\text{AgCl} \cdot 3\text{NH}_3$ , and with a higher pressure of the gas  $\text{AgCl} \cdot 3\text{NH}_3$ , the former with a tension of 93 mm., and the latter with a tension of about one atmosphere of ammonia at  $20^\circ$  (cf. p. 154). The bromide forms no compound in this way, but the iodide yields  $2\text{AgI} \cdot \text{NH}_3$ .

In consequence of the progressive insolubility, a cold solution of a bromide will convert the precipitate of silver chloride into bromide, and a soluble iodide will similarly transform the bromide or the chloride into iodide (cf. p. 405).

**Silver fluoride**  $\text{AgF}$  may be made by treating the oxide or carbonate with hydrofluoric acid:  $\text{H}_2\text{F}_2 + \text{Ag}_2\text{O} \rightarrow 2\text{AgF} + \text{H}_2\text{O}$ . The salt is very soluble and deliquescent.

**Complex Compounds of Silver.** — Silver chloride interacts easily with excess of ammonium hydroxide, giving the complex cation  $\text{Ag}(\text{NH}_3)_2^+$ . Under certain conditions octahedral crystals (Fig. 63, p. 172) of  $\text{AgCl}$  are deposited from the solution, and, under other conditions, crystals of the composition  $2\text{AgCl} \cdot 3\text{NH}_3$ . The bromide, which interacts less readily, gives the same complex ion. The iodide hardly interacts at all. **Ammonio-argentic-ion**  $\text{Ag}(\text{NH}_3)_2^+$ , in solutions of concentrations such as are commonly used (0.1*N* to *N*), gives about the same concentration of silver-ion  $\text{Ag}^+$  as does the bromide, and much more than the highly insoluble iodide (cf. p. 742). Hence the latter interacts very slightly with ammonium hydroxide, and can be precipitated in ammoniacal solution. All three of the insoluble halides dissolve in solutions of potassium cyanide and of sodium thiosulphate, as do also all the other insoluble silver salts. Usually an equivalent amount of the cyanide or thiosulphate suffices, but for solution of the sulphide an excess is required. With the cyanide, double decomposition gives first the insoluble silver cyanide  $\text{AgCN}$  which then interacts forming the soluble **potassium argenticyanide**  $\text{K} \cdot \text{Ag}(\text{CN})_2$ . The thiosulphate gives a solution from which crystals of a complex salt  $\text{Na}_3 \cdot \text{Ag}(\text{S}_2\text{O}_3)_2$  are obtained. The complex anion in the solution appears to be  $\text{Ag}(\text{S}_2\text{O}_3)_2^{=}$ . Since the iodide dissolves in the thiosulphate with considerable difficulty, we should infer that the complex thiosulphate anion gives about the same concentration of argentic-ion as does the iodide. An independent method of measuring the concentrations of argentic-ion in all the solutions places the compounds in the order of diminishing ability to give argentic-ion thus,  $\text{AgCl}$ ,  $\text{Ag}(\text{NH}_3)_2^+$ ,  $\text{AgBr}$ ,  $\text{Ag}(\text{S}_2\text{O}_3)_2^{=}$ ,  $\text{AgI}$ ,  $\text{Ag}(\text{CN})_2^-$ ,  $\text{Ag}_2\text{S}$ ,

and confirms the above inferences (see Concentration cells). The more active metals, like zinc and copper, displace silver from all solutions, whether the solutions contain simple or complex salts.

**Oxide of Silver.** — When sodium hydroxide is added to a solution of a salt of silver, a pale-brown precipitate is obtained, which, after being freed from water, is found to be  $\text{Ag}_2\text{O}$ . We should expect to obtain the hydroxide  $\text{AgOH}$  in this fashion, but it appears to be unstable. The aqueous solution of argentic oxide, however, is distinctly alkaline, and presumably therefore does contain the hydroxide:  $2\text{AgOH} \rightleftharpoons \text{Ag}_2\text{O} + \text{H}_2\text{O}$ . Silver oxide is formed by boiling silver chloride with caustic potash. Since the oxide is much more soluble than the chloride (see table), we should expect the reverse of the above action to be the normal one. Here, however, the excess of potassium hydroxide (hydroxide-ion) represses the ionization of the silver hydroxide and reverses the relations in regard to solubility (cf. p. 698).

Argentio oxide is an active basic oxide, and all the salts of silver are derived from it. When moist, it absorbs carbon dioxide from the air. Its solutions show concentrations of hydroxide-ion smaller, it is true, than equimolar solutions of the active bases, but considerably greater than similar solutions of ammonium hydroxide (p. 367). With ammonium hydroxide it forms the soluble ammonio-argentio hydroxide  $\text{Ag}(\text{NH}_3)_2\text{OH}$ , which is as active a base as is potassium hydroxide. The solution, when allowed to evaporate, deposits black crystals of an explosive substance whose composition has not been determined. This is "fulminating silver" (not to be confused with fulminate of silver  $\text{Ag.ONC}$ ). When the oxide is heated, it gives off oxygen, leaving metallic silver. The action is reversible (G. N. Lewis) and the dissociation pressure of the oxygen is 20.5 atmospheres at  $302^\circ$ . At a higher pressure than this (at  $302^\circ$ ), therefore, oxygen will combine with silver.

**Silver Nitrate  $\text{AgNO}_3$ .** — This salt is obtained by treating silver with aqueous nitric acid:



From the solution, colorless rhombic crystals (Fig. 14, p. 19) isomorphous with those of potassium nitrate (Fig. 71, p. 173) are deposited. These melt at  $208.6^\circ$ . Thin sticks made by casting (lunar\* caustic)

\* (Lat.) *luna* (the moon), the alchemical name for silver.



are used to cauterize sores, because the substance combines with proteins to form insoluble compounds. When commercial silver, containing copper, is used to make silver nitrate, the solution is evaporated to dryness and heated at  $250^{\circ}$  until the nitrate of copper has all been decomposed. At this temperature the silver salt is unaffected and, when cool, can be separated from the insoluble cupric oxide by extraction with water.

The aqueous solution is *neutral*. The pure salt is not affected by light, but when deposited on cloth, on the skin of the fingers, or on the mouth of the reagent bottle, it is converted into the chloride, and from this, in turn, silver is liberated. For this reason it is an ingredient in **marking-inks**. The dry compound combines with ammonia, giving  $\text{AgNO}_3 \cdot 3\text{NH}_3$ . When added to an aqueous solution, ammonium hydroxide produces, first a faint precipitation of the oxide, and then the soluble complex salt  $\text{Ag}(\text{NH}_3)_2 \cdot \text{NO}_3$ .

**Other Salts of Silver.** — **Silver peroxidate**  $\text{Ag}_2\text{O}_2$  (cf. p. 318) is formed by the action of ozone on silver. In the electrolysis of silver nitrate a deposit of shining black crystals ( $3\text{Ag}_2\text{O}_2 \cdot \text{AgNO}_3 \cdot 2\text{O}$ ) is formed on the positive electrode. When they are boiled with water, oxygen is given off, silver nitrate dissolves, and the peroxidate is deposited as a gray powder. **Silver carbonate**, the neutral salt  $\text{Ag}_2\text{CO}_3$ , and not a basic carbonate, is precipitated from solutions of salts of silver by soluble carbonates. It is slightly yellow in color. With water it gives a faint alkaline reaction and, like calcium carbonate, is soluble in excess of carbonic acid (p. 705). When heated, the carbonate decomposes, leaving metallic silver. Other compounds of silver, for example, the chloride, when heated in a crucible with sodium carbonate give this salt by double decomposition, and hence are finally reduced to a button of metallic silver. The **sulphate**  $\text{Ag}_2\text{SO}_4$  is made by the action of concentrated sulphuric acid on the metal. It is not very soluble in water, and crystallizes in rhombic prisms isomorphous with anhydrous sodium sulphate. When it is mixed with a solution of aluminium sulphate (*q.v.*), octahedral crystals of **silver-alum**  $\text{Ag}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  are obtained. **Silver sulphide**  $\text{Ag}_2\text{S}$  is precipitated by hydrogen sulphide from solutions of all silver compounds, whether free acids are present or not, and irrespective of the form in which the silver is combined. *Excess* of potassium cyanide, however, prevents its precipitation from the argenticyanide. The sulphide is formed by the action of metallic silver on alkaline hydrosulphides, and this interaction forms the

basis of the "hepar" test for sulphur (p. 441). Silver **orthophosphate**  $\text{Ag}_3\text{PO}_4$  (yellow), **arsenate**  $\text{Ag}_3\text{AsO}_4$  (brown), and **chromate**  $\text{Ag}_2\text{CrO}_4$  (crimson) are produced by precipitation, and their distinctive colors enable us to use silver nitrate in analysis as a reagent for identifying the acid radicals.

**Electroplating.** — The process is similar to the electro-déposition of copper (p. 747). The article to be plated is cleaned with extreme care and attached to the negative wire. A plate of silver forms the positive electrode and, since simple salts of silver do not give coherent deposits, the bath is a solution of potassium argenticyanide. The potassium-ion  $\text{K}^+$  migrates to the negative wire, and since potassium requires a much greater E.M.F. for its liberation than does silver, silver is there deposited from the trace of silver-ion given by the complex silver ions in the neighborhood:



The potassium cyanide remains in solution. At the positive electrode silver goes into solution in equivalent amount giving argenticion, and the above equations are reversed.

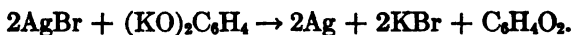
Mirrors are silvered through the reduction of ammonio-silver nitrate by organic compounds such as potassium-sodium tartrate (Rochelle salt), glycerine, formaldehyde  $\text{CH}_2\text{O}$  (formalin), or grape sugar:  $4\text{AgOH} + \text{CH}_2\text{O} \rightarrow 3\text{H}_2\text{O} + 4\text{Ag} \downarrow + \text{CO}_2$ . On a small scale, dilute silver nitrate is mixed with ammonium hydroxide until the solution is clear, and then a little caustic potash, a few more drops of ammonia, and finally a very little glycerine are added. A watch-glass floated on this mixture quickly acquires a deposit of silver. The film of silver is washed, dried, and varnished.

**Photography.** — Bromo-gelatine dry plates are made by preparing an emulsion of gelatine to which silver nitrate and a slight excess of ammonium bromide have been added. After the emulsion has been kept warm until the precipitate of silver bromide has coagulated into small granules ("ripening"), it is allowed to solidify. It is then cut up, and the ammonium nitrate is washed out with water. After drying and remelting, the emulsion is finally applied to plates of glass or films of celluloid. The excess of ammonium bromide and the ripening both increase the subsequent sensitiveness of the plates. Scott Archer (1850) first suspended the silver halide in a jelly (collodion).

After **exposure**, often for only a fraction of a second, there is no visible alteration in the film. The image is **developed**. Chemically, this consists in reducing the silver bromide to metallic silver by means of reducing agents. While the whole of the halide upon the plate is reducible, if the reducing agent is kept upon it for a sufficient length of time, the parts reached by the light are affected *first*, and with a speed proportional to the intensity of the illumination undergone by each part. The reducing agent is poured off when sufficient "contrast" between the parts variously illuminated has been attained. Development was discovered by Talbot (1837), or rather by his cat, which upset an extract of nut-galls on some half-exposed papers covered with silver chloride. The unreduced silver bromide is then dissolved out with sodium thiosulphate ("hyposulphite of soda" or "hypo"), first used by Sir John Hershell (1840), and the silver image is thus saved from obliteration by the silver that would be deposited if the plate were to be brought into the light without this treatment (**fixing**). The result is a "negative," as the parts brightest in the object are now opaque, and the darkest parts of the object are transparent.

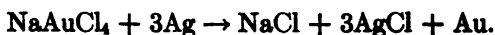
The gelatine is the sensitizing substance, and promotes the dissociation of the silver bromide:  $2\text{AgBr} \rightleftharpoons 2\text{Ag} + \text{Br}_2$ , which is a reversible action, by combining with the bromine. Potassium bromide is added to the developer if the plate has been over-exposed. This restrains the development, by rendering the silver bromide less soluble (*cf.* p. 698).

A common developer is the potassium salt of hydroquinone  $\text{C}_6\text{H}_4(\text{OH})_2$ , which gives quinone  $\text{C}_6\text{H}_4\text{O}_2$ :



An alkaline solution of the sodium salt of pyrogalllic acid is often used.

In **printing**, the light and dark are again reversed, the denser parts of the negative protecting the compounds on the paper below it from action, and leaving them white. Either "bromide" papers (such as **velox**, invented by Baekeland), which require only brief exposure and are developed like the plate, are used, or silver chloride is the sensitive substance, and prolonged exposure to light is allowed to liberate the proper amount of silver. The operation of **fixing** is performed as before. In **toning** chloride papers, a solution of sodium chloraurate is employed. A portion of the silver dissolves, **displacing** gold (p. 404), which is deposited in its place:



The thin film of gold gives a richer color to the print. In platinum toning, potassium chloroplatinite  $K_2PtCl_4$  is similarly used.

Many other actions are utilized in photography. Thus, ferric oxalate is reduced by light to ferrous oxalate:  $Fe_2(C_2O_4)_3 \rightarrow 2FeC_2O_4 + 2CO_2$ . When paper coated with a solution of the former, or with a mixture of ferric chloride and ammonium oxalate, is used for printing, the pale-yellow ferric salt loses its color where it has been turned into the ferrous salt. If the paper is then dipped in a solution of ferricyanide of potassium  $K_3Fe(CN)_6$  the ferrous salt precipitates the insoluble and deep-blue ferrous ferricyanide  $Fe_3[Fe(CN)_6]_2$ , while the unchanged ferric salt simply gives a soluble brown substance, which can be washed out. For regular **blue prints** ammonium-ferric citrate is employed instead of the oxalate. If the above paper, after printing, is dipped in potassium chloroplatinite (or has been coated with this salt at the same time that it received the ferric oxalate), and is then dipped in potassium oxalate solution, the latter dissolves the insoluble ferrous oxalate, and the potassium-ferrous oxalate reduces the platinum compound, giving a **platinum print**:



We have already seen (p. 581) that light of short wave-length — blue and violet — has the greatest effect upon silver halides. The time, in seconds, required for equal effects is approximately: violet 15, blue 29, green 37, yellow 330, red 600. Hence objects showing to the eye a variety of colors are entirely misrepresented, as regards the relative brightness of their parts, by photography. Now the important fact, in this connection is, that only that part of the light which is absorbed in traversing the film, and not that which is scattered or transmitted, can be used for chemical change. Hence, dipping plates in solutions of substances capable of absorbing yellow and red radiations causes them to absorb more of the energy of these photographically weakest radiations, and to give greater chemical action in response to them. This partially restores the balance. Such plates are called **orthochromatic**, and are backed with substances like eosin (used also in making red ink) or cyanine.

**Analytical Reactions of Silver Compounds.** — Argentio-ion  $Ag^+$  is colorless. Many of its compounds are insoluble, the precipitation of the chloride, which is insoluble in dilute acids, being used as a test. Mercurous chloride and lead chloride are also white and insoluble, but, in ammonium hydroxide, silver chloride dissolves,

mercurous chloride (*q.v.*) turns black, and lead chloride, which is also soluble in hot water, is not altered in color. With excess of ammonium hydroxide, silver salts give the complex cation  $\text{Ag}(\text{NH}_3)_2^+$  and, from solutions containing silver in this form, only the iodide and sulphide can be precipitated. Sodium thiosulphate and potassium cyanide dissolve all silver salts, giving salts of complex acids with silver in the anion (p. 752). Zinc displaces silver from all forms of combination.

### GOLD AU

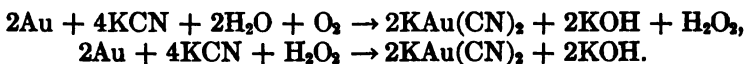
**Chemical Relations of the Element.** — This element forms two very incomplete series of compounds corresponding, respectively, to aurous and auric oxides,  $\text{Au}_2\text{O}$  and  $\text{Au}_2\text{O}_3$ . The former is a feebly basic oxide, the latter acid-forming. No simple salts with oxygen acids are stable. All the compounds of gold are easily decomposed by heat with liberation of the metal. All other common metals displace gold from solutions of its compounds (p. 404). Mild reducing agents likewise liberate gold. The element enters into many complex anions (p. 649).

**Occurrence and Metallurgy.** — Gold is found chiefly in the free condition disseminated in veins of quartz, or mixed with alluvial sand. Small quantities are found also in sulphide ores of iron, lead, and copper. Telluride of gold (sylvanite), in which silver takes the place of part of the gold  $[\text{Au}, \text{Ag}]\text{Te}_2^*$ , is found in Colorado. This mineral when heated loses its tellurium, and gold, alloyed with silver, remains.

From the alluvial deposits, gold is usually separated by washing in a cradle (densities, gold 19.32, rock about 2.6), as in the Klondyke. Quartz veins, which in the Transvaal Colony reach a thickness of a meter and carry an average of 18 g. of gold per ton, are mined, and the material is pulverized with stamping machinery. About 55 per cent of the gold is then separated by allowing the powdered rock to be carried by a stream of water over copper plates amalgamated with mercury. The gold dissolves in the latter, and is secured by removal and distillation of the amalgam. The finer particles contained in the sludge which runs off ("tailings") are extracted by adding a

\* Amongst minerals, mixed crystals of isomorphous salts are so commonly found that formulæ like the above are constantly used by mineralogists.  $[\text{Au}, \text{Ag}]\text{Te}_2$  indicates a mixture in varying proportions of the isomorphous tellurides  $\text{AuTe}_2$  and  $\text{AgTe}_2$ .

dilute solution of sodium cyanide (MacArthur-Forest process) and exposing the mixture to the air. Oxidation and simultaneous interaction with the cyanide give potassium aurocyanide  $\text{K.Au(CN)}_2$ . Hydrogen peroxide, which is formed in many oxidations by free oxygen, is produced also:



From this solution the gold is isolated, either by electrolysis, in which a plate of lead forms the cathode (and is subsequently cupelled: Siemens-Halske process), or in the form of a purple powder by precipitation with zinc. The same cyanide is used for another batch.

The gold is separated from ores containing silver, copper, lead, and other metals, and various methods of refining, mainly electrolytic, are used.

The world's production of gold during the first half of the nineteenth century averaged 27 tons annually. In 1897 it was 363 tons, and in 1899, 472.6 tons. This rapid increase in the supply of gold (which is our standard of value) has made it relatively cheaper, and other articles more expensive. In 1913 the total production was 680 tons, of which the Transvaal gave 40 per cent, the United States 20 per cent, and Australia 12 per cent, Russia 6 per cent, Mexico 4 per cent, Canada 4 per cent, India nearly 3 per cent.

**Properties of the Metal.** — Gold is yellow in color, and is the most malleable and ductile of all the metals. It melts at  $1063^\circ$ . Its density is 19.32. To give it greater hardness it is alloyed with copper, the proportion of gold being defined in "carats." Pure gold is "24-carat." British sovereigns are 22-carat and contain  $\frac{2}{3}$  of copper. American, French, and German coins are 21.6-carat, or 90 per cent gold. Silver takes the place of copper in Australian sovereigns.

Gold is not affected by free oxygen or by hydrogen sulphide. It does not displace hydrogen from dilute acids, nor does it interact with nitric or sulphuric acids or any oxygen acids, except selenic acid. It combines, however, with free chlorine (and bromine), and it therefore interacts with a mixture of nitric and hydrochloric acids (*aqua regia*), which gives off this gas (p. 537), giving chlorauric acid  $\text{H.AuCl}_4$  ( $= \text{HCl.AuCl}_3$ ). This happens, not because *aqua regia* is more active than are any of the substances it contains, but because it furnishes both the chlorine and the chloride-ion  $\text{Cl}^-$  required to pro-

duce the exceedingly stable (little dissociated) anion  $\text{AuCl}_4^-$ . Chlorine-water ( $\text{Cl}_2, \text{H}^+, \text{Cl}^-, \text{ClO}^-$ ) dissolves it also, for the same reason. Gold is the least active of the familiar metals.

**Compounds with the Halogens.** — **Chlorauric acid**, formed as above, is deposited in yellow, deliquescent crystals of  $\text{H.AuCl}_4 \cdot 4\text{H}_2\text{O}$ . The yellow sodium chloraurate  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ , obtained by neutralization of the acid, is used in photography (p. 756). The acid gives up hydrogen chloride when heated very gently, leaving the red, crystalline **auric chloride**  $\text{AuCl}_3$ . The tendency to form complex compounds is such, however, that when dissolved in water free from hydrochloric acid, this salt gives  $\text{H}_2\text{AuCl}_5\text{O}$ . Red crystals of  $\text{H}_2\text{AuCl}_5\text{O} \cdot 2\text{H}_2\text{O}$  are deposited by the solution. When auric chloride is heated to  $180^\circ$  **aurous chloride**  $\text{AuCl}$  and chlorine are formed. This salt is a white powder. It is insoluble in water, but in boiling water is converted quickly into auric chloride and free gold:  $3\text{AuCl} \rightarrow \text{AuCl}_3 + 2\text{Au}$ . When potassium iodide is added to a solution of chlorauric acid, or to sodium chloraurate, the yellow **aurous iodide** is precipitated:



The action is like that on cupric salts (p. 741), and for a similar reason, namely, that auric iodide is not stable.

**Other Compounds.** — When caustic alkalies are added to chlorauric acid, or to sodium chloraurate, **auric hydroxide**  $\text{Au}(\text{OH})_3$  is precipitated. This substance is an acid, and interacts with excess of the base, forming **aurates**. These are derived from met-auric acid ( $\text{Au}(\text{OH})_3 - \text{H}_2\text{O} = \text{HAuO}_2$ ), as, for example, **potassium aurate**  $\text{K.AuO}_2 \cdot 3\text{H}_2\text{O}$ . This salt interacts by double decomposition, giving, for instance, with silver nitrate, the insoluble **silver aurate**  $\text{AgAuO}_2$ . Its solution is alkaline in reaction, a fact which shows that auric acid is a weak acid (cf. p. 648). **Auric oxide**  $\text{Au}_2\text{O}_3$  is a brown, and **aurous oxide**  $\text{Au}_2\text{O}$  is a violet powder. With hydrochloric acid the latter gives chlorauric acid and free gold.

On account of its reducing action, hydrogen sulphide precipitates from chlorauric acid a dark-brown mixture containing much **aurous sulphide**  $\text{Au}_2\text{S}$  and free sulphur, as well as some **auric sulphide**  $\text{Au}_2\text{S}_3$ . The sulphides interact with alkali sulphides, giving complex **sulphaurites** and **sulphaurates**, such as  $\text{K}_3\text{AuS}_2$  ( $= 3\text{K}_2\text{S}, \text{Au}_2\text{S}$ ) and  $\text{KAuS}_3$ .

(=  $K_2S_2Au_2S_8$ ), which are soluble (p. 649, and see Tin, Arsenic, and Antimony).

The **aurocyanides**, like  $KAu(CN)_2$  (=  $KCN, AuCN$ ), and the **aurecyanides**, like  $KAu(CN)_4$  (=  $KCN, Au(CN)_3$ ), are formed by the action of potassium cyanide on aurous and auric compounds, respectively. They are colorless and soluble. Their solutions are used as baths, in conjunction with a gold anode, for electroplating.

**Analytical Reactions of Gold.** — The metallic "streak," produced by rubbing the metal on touchstone (Lydian stone, a black basalt), is not easily removed by nitric acid of sp. gr. 1.36 (57.5 per cent). The fineness of the gold can be determined by comparing the effect of the acid with that on streaks from pieces of gold of known fineness.

In **assaying**, the material containing the gold is heated with borax and lead in a small crucible (cupel) of bone-ash. The lead and copper are oxidized, and the oxides are absorbed by the cupel, leaving a drop of molten alloy of gold and silver. The cold button is flattened by hammering and rolling, and treated with nitric acid to remove the silver. The gold, which remains unattacked, is washed, fused again, and weighed. The acid will not interact with the silver and remove it completely if the quantity of gold exceeds 25 per cent. When the proportion of gold is greater than this, a suitable amount of pure silver is fused with the alloy ("quartation").

**Exercises.** — 1. How much copper will be deposited per hour on each sq. cm. of an electrode immersed in cupric sulphate solution when the current density is  $\frac{1}{2}$  ampere per sq. cm. (p. 357)? How much copper would be obtained under the same conditions from a cuprous salt?

2. Write equations for the interactions, (a) of salt water and oxygen with copper (p. 738), (b) of ferrous oxide and sand (p. 737), (c) of verdigris, arsenious acid, and acetic acid (p. 745).

3. Write the formulæ of the basic chloride, nitrate, carbonate, and sulphate of copper as if these substances were composed of the normal salt, the oxide and water (p. 738).

4. What may be the formula of the compound of cupric hydroxide and sodium tartrate (p. 744)?

5. Can you develop any relation between the facts that solutions of cupric salts are acid in reaction and that they give basic carbonates by precipitation?



6. Formulate the action of potassium cyanide in dissolving cupric hydroxide and cuprous sulphide, assuming that potassium cuprocyanide is formed.

7. How should you set about making cupric orthophosphate (in solution), ammonium cuprocyanide, and lead cuprocyanide?

8. Write the formulæ of some of the double salts analogous to potassium-cupric sulphate (p. 746).

9. What chemical reagents are present in a Bunsen flame? If borax beads were made in the oxidizing flame with cupric chloride, cuprous bromide, and cupric sulphate, severally, what actions would take place?

10. If the solubility ratio of silver in zinc and in lead were 1000 : 1, and 2 per cent of zinc were used, what proportion of the total silver would be secured by Parke's method?

11. Which is more stable, (a) silver sulphate or cupric sulphate, (b) silver nitrate or cupric nitrate? To what salts are the silver compounds in this respect more closely allied?

12. Write the equations for the interaction of, (a) silver and concentrated sulphuric acid, (b) silver chloride and sodium carbonate, when heated strongly, (c) sodium thiosulphate and silver bromide, (d) potassium ferricyanide and ferrous oxalate.

13. What reagents should you use to precipitate the phosphate, arsenate, and chromate of silver?

14. Write the equations for the interactions of, (a) gold and selenic acid, in which selenious acid is formed, (b) potassium hydroxide and auric hydroxide, (c) potassium cyanide and sodium chloraurate.

15. In what respects are the elements of this family distinctly metallic, and in what respects are they allied to the non-metals (p. 645)?

16. Collect all the evidence tending to show that the cuprous compounds are more stable than the cupric.

17. Describe in terms of the categories used by the phase rule the systems, (a) cupric nitrate and water at  $24.5^{\circ}$  and (b) silver iodide at  $146^{\circ}$ .

18. Make a classified list of the methods by which cupric compounds are transformed into cuprous, and *vice versa*.

19. Of which metals should it be possible to obtain colloidal suspensions in water, and of which not (p. 404)?

## CHAPTER XXXVII

### GLUCINUM, MAGNESIUM, ZINC, CADMIUM, MERCURY. THE RECOGNITION OF CATIONS IN QUALITATIVE ANALYSIS

**The Chemical Relations of the Family.** — The remaining elements of the third column of the periodic table, namely, glucinum or beryllium (Gl, or Be, at. wt. 9.1), magnesium (Mg, at. wt. 24.32), zinc (Zn, at. wt. 65.37), cadmium (Cd, at. wt. 112.4), and mercury (Hg, at. wt. 200.6), although all bivalent, do not form a coherent family. Glucinum and magnesium resemble zinc and cadmium, and differ from the calcium family, in that the sulphates are soluble, the hydroxides easily lose water leaving the oxides, the chlorides are comparatively volatile, and the metals are not rapidly rusted in the air and do not easily displace hydrogen from water. They resemble the calcium family, and differ from zinc and cadmium, in that the sulphides are hydrolyzed by water, the oxides are not reduced by heating with carbon, complex cations are not formed with ammonia, and the metals do not enter into complex anions. But glucinum differs from magnesium and resembles zinc in that its hydroxide is acidic as well as basic. This is not unnatural, since in the periodic system it lies between lithium, a metal, and boron, a non-metal. Mercury is the only member of the group that forms two series of compounds. These are derived (p. 488) from the oxides  $\text{HgO}$  and  $\text{Hg}_2\text{O}$ . Mercury approaches the noble metals in the ease with which its oxide is decomposed by heating, and in the position of the free element in the electromotive series.

The vapor densities of zinc, cadmium, and mercury show the vapors of these three metals to be monatomic.

The compounds of the metals of this family give no color to the borax bead.

#### GLUCINUM GL

**Chemical Relations of the Element.** — Glucinum (or beryllium) is bivalent in all its compounds. Its oxide and hydroxide are basic, and are also feebly acidic towards active bases (see Zinc hydroxide). On account of this fact and the extreme ease with which its

carbonate gives up carbon dioxide, in both of which respects it resembles aluminium, it was first thought to be trivalent. This made its atomic weight 13.6, the amount combining with one chemical unit of chlorine being 4.55. In the periodic system, however, there was a space for a bivalent element with the atomic weight 9.1 ( $= 2 \times 4.55$ ) between lithium and boron, and none for a trivalent element. Later (1884) Nilson and Pettersson determined the vapor density of the chloride and of certain organic compounds of the element, and found only 9.1 parts of glucinum in the molar weights of the compounds. The element derives its name from the sweet taste of its salts (Gk. γλυκός, sweet).

**The Metal and its Compounds.** — Glucinum occurs in beryl, a metasilicate of glucinum and aluminium  $\text{Al}_2\text{Gl}_3(\text{SiO}_3)_6$ . Specimens of beryl tinted green by the presence of a little silicate of chromium are known as **emeralds**. The metal may be obtained by electrolysis of the easily fusible double fluoride  $\text{GlF}_3 \cdot 2\text{KF}$ . In powdered form it burns when heated in the air. It displaces hydrogen from dilute acids, and also, when heated, from caustic potash:  $\text{Gl} + 2\text{KOH} \rightarrow \text{K}_2\text{GlO}_2 + \text{H}_2$ . The oxide interacts with acids and with strong bases. The salts give no color to the Bunsen flame.

## MAGNESIUM Mg

**Chemical Relations of the Element.** — Magnesium is bivalent in all its compounds. The oxide and hydroxide are basic exclusively. The element does not enter into complex cations or anions.

**Occurrence.** — Magnesium carbonate occurs alone as magnesite, and in a double salt with calcium carbonate  $\text{MgCO}_3 \cdot \text{CaCO}_3$  as dolomite. The sulphate and chloride are found as hydrates and as constituents of double salts (see below) in the Stassfurt deposits. Silicates are also common. Olivine is the orthosilicate  $\text{Mg}_2\text{SiO}_4$ . Serpentine is a hydrated disilicate,  $[\text{Mg}, \text{Fe}]_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , as is also meerschaum. Asbestos is an anhydrous silicate. Talc (soapstone) is  $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ . The element derives its name from Magnesia, a town in Asia Minor.

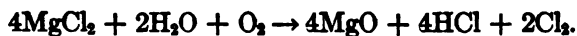
**The Metal.** — Magnesium is manufactured by electrolysis of dehydrated and fused carnallite  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ . The iron crucible in which the material is melted forms the cathode, and a rod of

carbon the anode. The metal is silver-white, and when heated can be pressed into wire and rolled into ribbon (m.-p. 651°, b.-p. 1100°). Commercial specimens of the latter often contain zinc.

Chemically the metal is less active than are the metals of the alkaline earths. It slowly becomes coated with a layer of a basic carbonate, which is non-coherent and so does not protect the metal from rusting completely. It displaces hydrogen slowly from boiling water, and does so rapidly if some ammonium chloride is added to interact with the layer of the hydroxide, and, of course, rapidly from cold, dilute acids. Magnesium burns in air with a white light, rich in rays of short wave-length such as act upon photographic plates (p. 757). The ash contains the nitride  $Mg_3N_2$ , as well as the oxide. The former interacts with water to give ammonia (p. 514). When the metal is heated with the oxides of boron, of silicon, and of many of the metals, it combines with the oxygen and liberates the other element.

Powdered magnesium is used in pyrotechny and, with potassium chlorate (10 : 17), in making flash-light powder for use in photography.

**Magnesium Chloride  $MgCl_2 \cdot 6H_2O$ .** — This salt occurs in salt deposits. It is a highly deliquescent compound, obtained also by evaporating an aqueous solution, and as carnallite  $MgCl_2 \cdot KCl \cdot 6H_2O$ . The latter is an important source of potassium chloride (p. 664), and almost all the magnesium chloride combined with it is thrown away. When the hexahydrate is heated, a part of the chloride is hydrolyzed, some magnesium oxide remaining, and some hydrogen chloride being given off. Sea-water cannot be used in ships' boilers because of the hydrochloric acid liberated by the magnesium chloride which the water contains. The salt forms a double chloride with ammonium chloride  $MgCl_2 \cdot NH_4Cl \cdot 6H_2O$  which is isomorphous with carnallite, and this salt can be dehydrated without hydrolysis of the chloride. Afterwards the ammonium chloride can be volatilized (p. 520). To utilize natural magnesium chloride, the manufacture of chlorine from it, by passing air and steam over the salt at a high temperature, has been attempted:

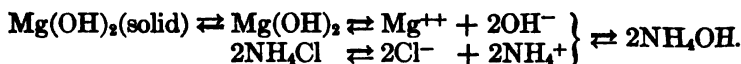


**The Oxide and Hydroxide.** — Magnesium oxide  $MgO$  is made by heating the carbonate, and is known as *calcined magnesia*. It is a white, highly infusible powder, and is used for lining electric fur-

naces and making crucibles. It combines slowly with water to form the hydroxide  $\text{Mg}(\text{OH})_2$ .

The **hydroxide** is found in nature as brucite. It is also precipitated from solutions of magnesium salts by alkalis. It is very slightly soluble in water, much less so than calcium hydroxide, but more so than are the hydroxides of zinc and the other heavy metals. The solution has a faint alkaline reaction. When magnesium chloride is added to the moist hydroxide, a hydrated basic chloride  $(\text{Mg}(\text{OH})_2)_x(\text{MgCl}_2)_y(\text{H}_2\text{O})_z$  is formed. The mixture, to which sawdust is sometimes added, is used as a plaster-finish in building.

Magnesium hydroxide is not precipitated by ammonium hydroxide when ammonium salts are present also. The ammonium salts, being highly ionized and giving a high concentration of ammonium-ion  $\text{NH}_4^+$ , repress the ionization of the feebly ionized ammonium hydroxide, and so reduce the concentration of hydroxide-ion which it furnishes. With the ordinary concentration of  $\text{Mg}^{++}$ , therefore, the amount of hydroxide-ion existing in presence of excess of a salt of ammonium is too small to bring the ion product  $[\text{Mg}^{++}] \times [\text{OH}^-]$  up to the value required for precipitation (p. 698). Conversely, magnesium hydroxide interacts with solutions of ammonium salts and passes into solution:

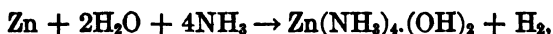


In presence of excess of ammonium chloride, the  $\text{OH}^-$  combines with  $\text{NH}_4^+$  to form molecular ammonium hydroxide, and the equilibria in the upper line are displaced forwards to generate a further supply of the  $\text{OH}^-$ . With sufficiently great concentration of the ammonium chloride, all the magnesium hydroxide may thus dissolve; with only a small excess, a condition of equilibrium with solid magnesium hydroxide is reached. The whole case is analogous to the interaction of acids with insoluble salts (p. 713). Magnesium *oxide* also dissolves in salts of ammonium. It gives first the hydroxide by interaction with the water.

**Magnesium Carbonates.**—The normal carbonate  $\text{MgCO}_3$  (magnesite) is found in nature. Only hydrated *basic* carbonates are formed by precipitation, and their composition varies with the conditions. The carbonate manufactured in large amounts and sold as **magnesia alba** is approximately  $\text{Mg}_3(\text{OH})_2(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$ . It

**Properties and Uses of the Metal.** — Zinc is a bluish-white, crystalline metal. When cold it is brittle, but at 120–150° it can be rolled into sheets between heated rollers and then retains its pliability when cold. At 200–300° the metal becomes once more brittle, at 119.4° it melts, and at 925° it boils. The vapor density at 1740° is 2.64 (air = 1), and the molecular weight, therefore,  $2.38 \times 28.955$  (p. 233) or 68.9. The gas is thus monatomic.

The metal burns in air with a greenish flame, giving zinc oxide. When cold it is not affected by dry air, but in moist air it is oxidized, and becomes covered with a firmly adhering, non-porous layer of basic carbonate which protects it from further action. The metal displaces hydrogen from dilute acids, but with pure specimens the action almost ceases in consequence of the formation of a layer of condensed hydrogen on the surface. Contact with a less electropositive metal, such as lead, iron, copper, or platinum, enables the action to go on, because the hydrogen is then liberated at the surface of the other metal (see Electromotive chemistry). Crude zinc contains lead and iron and is therefore more active than pure zinc. Zinc also attacks boiling alkalis, giving the soluble zincate (see below):  $\text{KOH} + \text{Zn} + \text{H}_2\text{O} \rightarrow \text{KHZnO}_2 + \text{H}_2$ . The action on ammonium hydroxide is slower and different in nature:

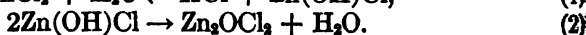
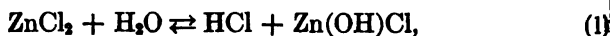


a complex cation being formed.

Sheet zinc, in consequence of its lightness (density 7), is used in preference to lead (density 11.5) for roofs, gutters, and architectural ornaments. Galvanized iron is made by dipping sheet iron, cleaned with sulphuric acid or the sand blast, into molten zinc. The latter, being more active (p. 404), is rusted instead of the iron, but the rusting is very slight. Objects of iron, cleaned and baked in zinc dust, also acquire a coating of zinc (sherardizing). Zinc is used also in batteries and for making alloys (p. 644). It mixes in all proportions with tin, copper, and antimony, but with lead (p. 749) and with bismuth separation into two layers occurs, each metal dissolving only a little of the other. The two different modes of behavior resemble those of alcohol and water (p. 179) and ether and water (p. 180), respectively.

**Zinc Chloride  $\text{ZnCl}_2$ .** — This salt is usually manufactured by treating zinc with *excess* of hydrochloric acid, evaporating the solution to dryness, and fusing the residue. When hydrochloric acid is

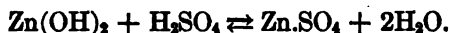
thus present, the chloride  $\text{ZnCl}_2$  is obtained. Evaporation of the pure aqueous solution, which is acid in reaction, results in considerable hydrolysis and formation of much of the basic chloride  $\text{Zn}_2\text{OCl}_2$ :



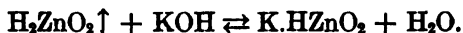
The salt is **used** in solid form as a caustic and, by injection of a solution into wood (e.g., railway sleepers), as a poison to prevent the growth of organisms which promote decay. In both cases the salt combines with proteins, forming solid products. The aqueous solution, being acid, is employed also for dissolving the oxides from surfaces which are to be soldered. The acid is reproduced by hydrolysis as fast as it is used, and finally the oxychloride remains (equation 1 above). The hot solution also gelatinizes and dissolves cellulose (cotton or paper), or probably takes it into colloidal suspension. When the solution is pressed through an orifice into alcohol, the cellulose is precipitated in the form of a thread. By carbonizing such threads, carbon filaments for incandescent lamps are made.

**Zinc Oxide and Hydroxide and the Zincates.**—The oxide  $\text{ZnO}$  is obtained as a white powder by burning zinc or by heating the precipitated basic carbonate. It turns yellow when heated, recovering its whiteness when cold, in the same way that mercuric oxide is brown whilst hot and bright red when cold. It is **used** in making a paint — zinc-white or Chinese white — which is not darkened by hydrogen sulphide. It is also used as a filler in rubber automobile tires. For filling teeth, dentists sometimes use a paste made by mixing the oxide with a strong solution of zinc chloride. It quickly sets to a hard mass of oxychloride.

The **hydroxide**  $\text{Zn(OH)}_2$  of zinc appears as a white, flocculent solid when alkalis are added to solutions of zinc salts. It interacts as a basic hydroxide with acids, giving salts of zinc:

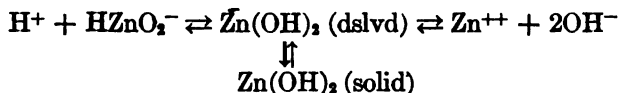


It also interacts with excess of the alkali employed to precipitate it, giving a soluble **zincate**, such as **potassium zincate**  $\text{KHZnO}_2$ :



Both actions are reversible, and the second requires a considerable excess of alkali for its completion: in fact, some of the zinc hydroxide

seems to be simply in colloidal suspension. It is evident that zinc hydroxide when in solution is ionized both as an acid and as a base:



The ionization as an acid is less than that as a base, but both are small. Addition of an acid like sulphuric acid, however, furnishes hydrogen-ion, the hydroxide ions combine with this to form water, and all the equilibria are displaced to the right. With a base, on the other hand, the hydrogen-ion is removed and the basic ionization simultaneously repressed, so that the equilibria are displaced to the left. Such a substance is called **amphoteric**.

Zinc hydroxide interacts with ammonium hydroxide, giving a soluble complex compound **ammonio-zinc hydroxide**  $\text{Zn(NH}_3)_4\text{(OH)}_2$ . The case is like those of copper (p. 743) and silver hydroxides (p. 753), and not like that of magnesium hydroxide (p. 766).

Compounds of zinc, when heated in the Bunsen flame with a salt of cobalt, give a **zincate of cobalt** (Rinmann's green)  $\text{CoZnO}_2$ .

Hydrogen sulphide precipitates zinc sulphide from solutions of zincates and from solutions containing ammonia, so that some zinc ions  $\text{Zn}^{++}$  are present in both.

**Carbonates of Zinc.** — The normal **zinc carbonate**  $\text{ZnCO}_3$  may be precipitated by means of sodium bicarbonate:



The normal carbonate of sodium, however, gives **basic carbonates**, such as  $\text{Zn}_2\text{(OH)}_2\text{CO}_3$ , which, as in the case of magnesium (p. 766), vary in composition according to the conditions.

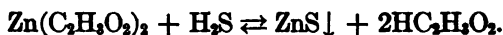
**Zinc Sulphate  $\text{ZnSO}_4$ .** — This salt is formed by oxidation when zinc-blende is roasted. It gives rhombic crystals of the hydrate  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . This, and the corresponding compounds of magnesium  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , of iron  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and of several other bivalent metals, are all isomorphous, and are known as **vitriols**. The zinc salt is **white vitriol**. Like Epsom salts, it is dehydrated by stages, the last molecule of water being difficult to remove. It is used in cotton-printing and as an eye-wash ( $\frac{1}{2}$  per cent solution).

The salt gives double salts with potassium or ammonium sulphate, of the form  $\text{ZnSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , which crystallize in the mono-

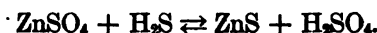


symmetric system, and are isomorphous with each other, and with double salts containing copper (p. 746), mercury ( $\text{Hg}^{\text{II}}$ ), iron ( $\text{Fe}^{\text{II}}$ ), magnesium, and other bivalent elements in place of the zinc. These compounds, unlike the complex cyanides, are almost completely decomposed in dilute solution (*cf.* p. 402).

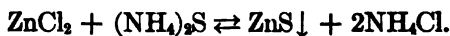
**Zinc Sulphide  $\text{ZnS}$ .** — This compound is the only familiar sulphide which is white. The yellow color of zinc-blende is caused by the presence of sulphide of iron. Zinc sulphide is more soluble in water than is sulphide of copper, and hence it interacts with excess of strong acids, and passes into solution. It is not soluble enough, however, to be much affected by weak acids like acetic acid. This sort of behavior is shown also by calcium oxalate (p. 713), and was discussed fully in that connection. Zinc sulphide is thus capable of being almost completely precipitated when acetic acid is present, or when hydrogen sulphide is led into a solution of the acetate of zinc:



But when an active acid is present, or is formed, the sulphide is precipitated very incompletely or not at all, the action being highly reversible:



There are thus two ways of obtaining the sulphide by precipitation. A soluble sulphide causes it to be thrown down completely because no acid is liberated in the action:



The other method is to add sodium acetate to the solution of the salt, and then lead in hydrogen sulphide. The acid, liberated by the action upon the salt, interacts with the sodium acetate, giving a neutral salt of sodium and acetic acid, and the zinc sulphide is not much affected by the latter. In terms of ions, the hydrogen-ion, liberated as the hydrogen sulphide interacts with the zinc salt, combines with acetate-ion introduced by the sodium acetate, and gives the little-ionized acetic acid. For *uses*, see lithopone (p. 730).

**Analytical Reactions of Zinc Salts.** — Zinc sulphide is precipitated by the addition of ammonium sulphide to solutions of zinc salts and of zincates. Sodium hydroxide gives the insoluble hydroxide, which, however, interacts with excess of the alkali, giving the

soluble zincate of sodium. Compounds of zinc, when heated on charcoal with cobalt nitrate, give Rinmann's green (p. 771).

#### CADMIUM Cd

**Chemical Relations of the Element.** — This element is bivalent in all its compounds. Its oxide and hydroxide are basic exclusively, and the salts are not hydrolyzed by water. It enters into complex compounds having the ions  $\text{Cd}(\text{NH}_3)_4^{++}$ ,  $\text{Cd}(\text{CN})_4^{=}$ , and  $\text{CdI}_4^{=}$ .

**The Metal.** — Aside from the rare mineral greenockite  $\text{CdS}$ , cadmium is found only in small amounts (about 0.5 per cent), as carbonate and sulphide, in the corresponding ores of zinc. During the reduction, being more volatile than zinc, it distils over first (b.p.  $778^\circ$ ). The metal is white, and is much more malleable than is zinc. It melts at  $320^\circ$ .

It displaces hydrogen from dilute acids, but is itself displaced from solutions of its compounds by zinc, since it is less electro-positive. It is **used** in making fusible alloys.

**Compounds of Cadmium.** — The chloride  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$  is efflorescent and is not hydrolyzed during dehydration or in solution. Zinc chloride (p. 770) is deliquescent and is easily hydrolyzed. The halides are less ionized than are the corresponding compounds of most other metals. The iodide  $\text{CdI}_2$ , in particular, seems to exist in solution as  $\text{Cd} \cdot \text{CdI}_4$ , and the complex anion gives little ionic cadmium. On account of this fact even the sulphide cannot be precipitated completely from a solution of the iodide. Conversely, hydriodic acid dissolves the sulphide to a much greater extent than do other acids (see below).

The white hydroxide is made by precipitation, and interacts as a basic hydroxide with acids, but not at all with bases. It dissolves in ammonium hydroxide, however, forming  $\text{Cd}(\text{NH}_3)_4(\text{OH})_2$ . The oxide  $\text{CdO}$  is a brown powder, obtained by heating the hydroxide, carbonate, or nitrate, or by burning the metal.

The sulphate crystallizes as  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ , and is not isomorphous with the sulphates of zinc and magnesium. Soluble carbonates throw down the normal carbonate  $\text{CdCO}_3$ , and not a basic carbonate.

Hydrogen sulphide precipitates the yellow sulphide  $\text{CdS}$  even from acid solutions of the salts. The substance is used as a pigment.

The sulphide of cadmium, however, is less insoluble in water than are the sulphides of copper and mercury, and therefore cannot be precipitated from a strongly acid solution (*e.g.*,  $\text{HCl} > 0.3N$ ).

**The Solubilities of the Sulphides of the Metals.**—The reader will remember the order of solubility of the metallic sulphides more easily if he notes that it is practically the same as the order of activity of the free metals (p. 404). Thus, the sulphides down to that of aluminium are dissolved by water ( $\text{K}_2\text{S}$  and  $\text{Na}_2\text{S}$ ), or are decomposed by water ( $\text{BaS}$ ,  $\text{SrS}$ ,  $\text{CaS}$ ,  $\text{MgS}$ ,  $\text{Al}_2\text{S}_3$ ). The hydroxides formed, being soluble (except  $\text{Al}(\text{OH})_3$ ), the whole dissolves except in the case of  $\text{Al}_2\text{S}_3$ . Ferrous sulphide is insoluble in water, but is soluble enough to interact with (and dissolve in) dilute acids to some extent, even with a feeble one like acetic acid. Zinc sulphide requires a dilute *active* acid; cadmium sulphide requires a higher concentration of an active acid, as do also  $\text{CoS}$  and  $\text{NiS}$ ; cupric sulphide requires an oxidizing acid like hot nitric acid; and mercuric sulphide resists even this.

The molar solubilities of the sulphides in water have not been determined with great exactness, but are approximately as follows:

$\text{MnS}$ , 0.0 <sub>26</sub>	$\text{PbS}$ , 0.0 <sub>12</sub> 2	$\text{Ag}_2\text{S}$ , 0.0 <sub>12</sub> 2
$\text{FeS}$ , 0.0 <sub>6</sub> 6	$\text{CdS}$ , 0.0 <sub>14</sub> 7	$\text{CuS}$ , 0.0 <sub>1</sub> 1
$\text{ZnS}$ , 0.0 <sub>11</sub> 7	$\text{Bi}_2\text{S}_3$ , 0.0 <sub>13</sub> 3	$\text{HgS}$ , 0.0 <sub>3</sub> 3

**Analytical Reactions of Cadmium Compounds.**—The cadmium ion  $\text{Cd}^{++}$  is bivalent and colorless. The yellow cadmium sulphide is precipitated by hydrogen sulphide, even from acid solutions of the salts. It is also precipitated from solutions containing the complex cation  $\text{Cd}(\text{NH}_3)_4^{++}$  and the complex anion  $\text{Cd}(\text{CN})_4^-$ , as, for example, from a solution made by adding excess of potassium cyanide to cadmium chloride solution ( $\text{K}_2\text{Cd}(\text{CN})_4$ ). The latter property enables cadmium to be separated from copper (p. 746). The white hydroxide is thrown down by sodium hydroxide, and is not soluble in excess of this reagent. It is not formed from solutions containing the  $\text{Cd}(\text{NH}_3)_4^{++}$  and  $\text{Cd}(\text{CN})_4^-$  ions, and interacts with ammonium hydroxide to give the soluble  $\text{Cd}(\text{NH}_3)_4(\text{OH})_2$ . These and other precipitations are not complete when cadmium iodide  $\text{Cd.CdI}_4$  is used.

## MERCURY Hg

**Chemical Relations of the Element.** — Like copper, this element enters into two series of compounds, the mercurous  $\text{Hg}^{\text{I}}$  and the mercuric  $\text{Hg}^{\text{II}}$ , in which it is univalent and bivalent, respectively. The mercurous halides, like the cuprous halides (and the argentic halides), are insoluble in water and are decomposed by light. There are, however, stable mercurous as well as mercuric salts of oxygen acids. Both of the oxides,  $\text{Hg}_2\text{O}$  and  $\text{HgO}$ , are basic exclusively, but in a feeble degree. The hydroxides, like silver hydroxide, are not stable, and lose water, giving the oxides. The salts of both sets are markedly hydrolyzed by water, and basic salts are therefore common. No carbonate is known (cf. p. 656). Mercury enters into the anions of a number of complex salts, such as  $\text{HgCl}_4^{=}$ ,  $\text{HgI}_4^{=}$ ,  $\text{Hg}(\text{CN})_4^{=}$ , etc. It does not give complex cations with ammonia resembling those of cadmium, copper, and silver ( $\text{Cd}(\text{NH}_3)_4^{++}$ , etc.), from which ammonia is removed by heating, but instead forms a class of ammono-basic mercury compounds like  $\text{Hg}^{\text{II}}\text{NH}_2\text{Cl}$ , all of which are insoluble. The mercuric halides and cyanide show many peculiarities due to their being very little ionized. Salts as a class are highly ionized bodies, and those of mercury and, to a less degree, those of cadmium are the only conspicuous exceptions.

The mercury salts of volatile acids, like the corresponding salts of ammonium (p. 520), can all be volatilized completely. Mercury vapor and mercury compounds are **poisonous**, the soluble ones more markedly so than the insoluble ones.

The mercurous salts, as a rule, are formed when excess of mercury is employed, and mercuric salts when excess of the oxidizing acid or other substance is present. Reducing agents turn mercuric into mercurous salts, and oxidizing agents do just the reverse.

As in the case of the cuprous compounds, it is a question whether simple or multiple formulæ,  $\text{HgCl}$  or  $\text{Hg}_2\text{Cl}_2$ , etc., should be employed for mercurous salts. Pending the discovery of some basis for a decision, the simple formulæ are used here.

**Occurrence and Isolation of the Metal.** — Mercury occurs native and as red, crystalline cinnabar, mercuric sulphide  $\text{HgS}$ . The production (1913) in iron flasks (75 lbs. each) is, Spain 43,800, Italy 29,500, Austria 26,720, United States 20,200, Mexico 4,410.

The liberation of the metal is easy, because, when roasted, the sulphide is decomposed, and the sulphur forms sulphur dioxide. The

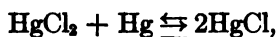
mercury does not unite with the oxygen, for the oxide decomposes (p. 17) at 400–600°:  $\text{HgS} + \text{O}_2 \rightarrow \text{Hg} + \text{SO}_2$ . In some places the ore is spread on perforated brick shelves in a vertical furnace, and the gases pass through tortuous flues in which the vapor of the metal condenses. The product is filtered through chamois-skin. For separation from metallic impurities, like zinc, arsenic, and tin, which are dissolved, it must be distilled. In the laboratory, where mercury finds many applications, it becomes impure with use, and then adheres to glass, and does not run freely in spherical droplets. For purification it is placed along with a little diluted nitric acid in a separatory funnel (Fig. 74, p. 180), and kept in continual agitation by means of a current of air drawn or blown through the mass. By this treatment, foreign metals, such as sodium or zinc, nearly all of which are much more active than mercury (*cf.* p. 404), are converted into nitrates. Pure, dry mercury can be drawn off, when needed, at the bottom. If a high degree of purity is required, the product must be distilled *in vacuo*.

**Physical Properties.** — Mercury or quicksilver (N.L. *hydrargyrum*, from Gk. *ὕδωρ*, water, and *ἀργυρος*, silver) is a silver-white liquid. At  $-38.9^\circ$  it freezes, and at  $357^\circ$  it boils. At ordinary temperatures it has a measurable vapor tension, at  $15^\circ$  0.0008 mm., and at  $100^\circ$  0.28 mm. The vapor is colorless, does not conduct electricity, and is monatomic. A gold-leaf suspended over mercury becomes amalgamated, since the solution of gold in mercury has a vapor tension smaller than that of pure mercury (p. 197).

On account of its high density (13.6, at  $0^\circ$ ) and low vapor tension, the metal is employed for filling barometers and manometers. Its uniform expansion favors its use in thermometers. The tendency to form amalgams, which it exhibits towards all the familiar metals with the exception of iron and platinum (both, however, are "wet" by it), is taken advantage of in various ways. Sodium amalgam (p. 684), which is solid when the sodium exceeds 2 per cent, and consists mainly of  $\text{NaHg}_2$ , behaves like free sodium, but with moderated activity. A layer of mercury on the zinc plates of batteries reduces the action of the acid on the zinc, while the cells are not in use. Mixtures of mercury with powdered tin, silver, and gold quickly form solid amalgams, and are used by dentists. The employment of mercury in the extraction of gold has been mentioned (p. 758. See also p. 750). Mirrors backed with a tin-mercury amalgam have been displaced by silvered mirrors (p. 755).

**Chemical Properties.** — When kept at a temperature near to its boiling-point, mercury combines slowly with oxygen. Its inactivity towards oxygen when cold places it next to the noble metals. On account of its general inactivity, it is used in the laboratory for confining gases. It does interact with hydrogen sulphide and hydrogen iodide, however (*cf.* Silver, p. 751). Mercury does not displace hydrogen from dilute acids (p. 404), but with oxidizing acids like nitric acid and hot concentrated sulphuric acid, the nitrates and sulphates are formed. With excess of mercury, the mercurous salts, and with excess of the hot acid, the mercuric salts, are produced. When triturated, so that the mercury is divided into minute droplets with relatively large surface, it is used in medicine (blue pills), and shows an activity which is entirely wanting in larger masses.

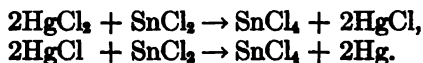
**Mercurous Chloride  $HgCl$ .** — This salt (**calomel**) is obtained as a white powder by precipitation from solutions of mercurous salts. It is manufactured by subliming mercuric chloride with mercury:



or more usually by subliming a mixture of mercuric sulphate, made as described above, with mercury and common salt. It is deposited on the cool part of the vessel as a fibrous crystalline mass. It is slowly affected by light just as is silver chloride. Here, however, the chlorine which is released combines with another molecule of the salt to form mercuric chloride. Since the vapor pressure of calomel reaches 760 mm. before the temperature has risen to the melting-point, the compound sublimes at atmospheric pressure without melting. Its vapor density corresponds to the formula  $HgCl$ , but the vapor was shown by Smith and Menzies to consist wholly of  $Hg + HgCl_2$ . The completeness of the dissociation was ascertained by measuring the partial pressures of the mercury and mercuric chloride in the vapor, and finding that together they equalled the total dissociation pressure. The action is reversed when the temperature falls (*cf.* Ammonium chloride, p. 720). The substance is used in medicine on account of its tendency to stimulate all organs producing secretions.

**Mercuric Chloride  $HgCl_2$ .** — By direct union with chlorine the mercuric salt, **corrosive sublimate**  $HgCl_2$ , is formed. It is usually manufactured by subliming mercuric sulphate with common salt, and crystallizes in white, rhombic prisms. It melts at  $265^\circ$  and boils at  $307^\circ$ . The solubility at  $20^\circ$  is 7.4 : 100 Aq, and at  $100^\circ$ , 54 : 100

Aq. It is more soluble in alcohol and in ether. The aqueous solution is slightly acid in reaction. The salt is easily reduced to mercurous chloride. When excess of stannous chloride is added to the solution, the white precipitate of calomel, first formed, passes into a heavy gray precipitate of finely divided mercury:



The halides of mercury are very little ionized in solution, the bromide and iodide even less so than the chloride. Hence these salts are little affected by sulphuric acid or nitric acid. For example, the chlorine and nitrosyl chloride which hydrochloric acid forms with the nitric acid (p. 537) are not observed when mercuric chloride is added to nitric acid. On this account, too, the hydrolysis of the chloride is much less than that of the nitrate. There is a tendency also to the formation of complex salts, so that the addition of sodium chloride increases the solubility in water and renders the solution neutral,  $\text{NaHgCl}_3$  being formed. The complex salts, like  $\text{K.HgCl}_3, \text{H}_2\text{O}$ ,  $\text{H}_2.\text{HgCl}_4, 7\text{H}_2\text{O}$ , and  $\text{NH}_4.\text{HgCl}_3, \text{H}_2\text{O}$ , are easily made by crystallization from solution. The anions are relatively highly ionized, however, and the behavior is intermediate between that of complex salts and double salts (p. 649).

Corrosive sublimate, when taken internally, causes death. The variable meaning of the word "poisonous" is well illustrated in this case. The mercuric chloride does not act as a direct poison. It causes changes in the cells of the kidneys so that, after about two weeks, the waste products from the system (urea, etc.) can no longer be eliminated, and death occurs from a sort of autointoxication. A very dilute solution is used in surgery to destroy lower organisms and thus prevent infection of wounds. The pharmaceutical tabloids of mercuric chloride contain sodium chloride, because, although the latter diminishes the activity of the compound, it also does away with the formation of insoluble, basic chlorides and hastens solution. Mercuric chloride acts also as a preservative of zoological materials, forming insoluble compounds with proteins, and preventing their decay. For the same reason, albumin (white of an egg, a mixture of proteins) is given as an antidote in cases of sublimate poisoning.

**The Iodides of Mercury.** — Mercurous iodide  $\text{HgI}$  is formed by rubbing iodine with excess of mercury. It also appears as a green-

ish-yellow precipitate when potassium iodide is added to a solution of a mercurous salt. The compound decomposes spontaneously into mercury and mercuric iodide. The decomposition is much hastened by the use of excess of potassium iodide, which combines with and removes the mercuric iodide (see below):



**Mercuric iodide**  $\text{HgI}_2$  is obtained by direct union of mercury with excess of iodine, or by addition of potassium iodide to a solution of a mercuric salt. It is a scarlet powder, insoluble in water, but soluble in alcohol and ether. It interacts with excess of potassium iodide, forming the soluble, colorless **potassium mercuri-iodide**  $\text{K}_2\text{HgI}_4$  with which many precipitants fail to give mercury compounds. When heated above  $128^\circ$  it turns into a yellow modification, and at  $223^\circ$  this new form melts. On being cooled, the liquid freezes first in the tetragonal yellow form, and below  $128^\circ$ , especially if touched with a glass rod, it changes into the red, monoclinic variety with evolution of heat. Sulphur (p. 411) and ammonium nitrate (p. 679) show similar transition points. When the vapor of the compound is cooled, it first forms thin scales of the yellow form, which is the unstable one at low temperatures, and these turn red when touched. Similarly, precipitation gives first the yellow variety, which presently becomes red (*cf.* Transformation by steps, p. 544).

**The Oxides.**—When bases (excepting ammonium hydroxide, see p. 781) are added to solutions of mercurous salts, the brownish-black **mercurous oxide**  $\text{Hg}_2\text{O}$  is thrown down. The hydroxide is doubtless formed transitorily and then loses water (*cf.* Silver oxide, p. 753). Under the influence of light or gentle heat ( $100^\circ$ ), this compound resolves itself into mercuric oxide and mercury.

**Mercuric oxide**  $\text{HgO}$  is formed as a red, crystalline powder, when mercury is heated in air near to  $357^\circ$ , but is usually made by decomposing the nitrate. Commercial specimens, incompletely decomposed, thus frequently give the brown nitrogen tetroxide when heated. It is formed also as a yellow powder by adding bases (excepting ammonium hydroxide, see p. 781) to solutions of mercuric salts. It is contended by some chemists that the difference in activity between the red and yellow forms is due solely to the finer state of division of the latter, and by others it is maintained that the substance is dimorphous (p. 412) and that two distinct varieties exist.



**The Nitrates.** — The mercurous salt  $\text{HgNO}_3 \cdot \text{H}_2\text{O}$  is formed by the action of cold, diluted nitric acid upon *excess* of mercury. It forms monoclinic crystals. It is hydrolyzed, slowly by cold, and rapidly by warm water, giving an insoluble basic nitrate:



On this account a clear solution can be made only when some nitric acid is added. Free mercury is also kept in the solution to reduce mercuric nitrate, which is formed by atmospheric oxidation:



**Mercuric nitrate**  $\text{Hg}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$  is produced by using excess of warm, concentrated nitric acid. It forms rhombic tables. The aqueous solution is strongly acid, and deposits a yellowish, crystalline, basic nitrate  $\text{Hg}_2(\text{OH})_2\text{O}(\text{NO}_3)_2$ . The hydrolysis is reversed by adding nitric acid.

**Sulphides of Mercury.** — **Mercurous sulphide**  $\text{Hg}_2\text{S}$  is formed by precipitation from mercurous salts, but is stable only below  $-10^\circ$ . Above  $-10^\circ$  it decomposes into mercury and mercuric sulphide.

Crystallized **mercuric sulphide**  $\text{HgS}$  occurs as cinnabar, and is red. When formed by precipitation with hydrogen sulphide, or by rubbing together mercury and sulphur, it is black and amorphous. By sublimation, in the course of which it dissociates, the black form gives the red, crystalline one. When allowed to stand under a solution of sodium sulphide, the black form is slowly transformed into the red. This shows that the red form is the more stable, possesses less energy, and is less soluble at ordinary temperatures. The change is effected by intermediate formation of a complex sulphide, the solution, when saturated toward the less stable black sulphide, being supersaturated toward the more stable red one. A white, crystalline sodium mercuri-sulphide  $\text{Na}_2\text{HgS}_2 \cdot 8\text{H}_2\text{O}$  can be obtained from the solution.

The black and the red varieties do not interact even with boiling nitric acid, which oxidizes most sulphides readily. They are, therefore, less soluble in water than is cupric sulphide (pp. 421, 774). They are attacked, however, by *aqua regia*, because of the formation of the negative ion (see gold, p. 759) of a complex salt  $\text{H}_2\text{HgCl}_4$  ( $=2\text{HCl}, \text{HgCl}_2$ ).

The red form of the sulphide is used in making paint (**vermillion**). The color is more permanent than that of red lead  $\text{Pb}_3\text{O}_4$ , because reducing gases (e.g.,  $\text{SO}_2$ ), acids (e.g.,  $\text{H}_2\text{SO}_4$ ), and hydrogen sulphide,

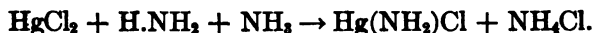
which are present in the air, do not affect it. It is not stable, however, when applied to metals, since iron, zinc, etc., all displace mercury from combination, and in these cases red lead is preferred.

**Mercuric Cyanide  $Hg(NC)_2$ .** — This salt is made by treating precipitated mercuric oxide with hydrocyanic acid, and is obtained in square-prismatic crystals. When heated it gives off cyanogen:  $Hg(NC)_2 \rightarrow Hg + C_2N_2$ , and is a convenient source of this gas (p. 625). The compound is soluble in alcohol, ether, and water. In solution in water it is so little ionized that the freezing-point of the solution is normal (p. 336), and many reagents fail to show the presence of either ion. Thus, with silver nitrate no silver cyanide is precipitated, and with a base no mercuric oxide. With potassium cyanide it forms a complex cyanide  $K_2.Hg(CN)_4$ . Hydrogen sulphide throws down the sulphide from both the simple and the complex cyanides.

**The Fulminate and Thiocyanate.** — **Mercuric fulminate**  $Hg(ONC)_2$  is obtained as a white precipitate when mercury is treated with nitric acid, and alcohol is added to the solution. It decomposes suddenly when struck, and is used in making percussion caps.

The **thiocyanate**  $Hg(NCS)_2$  is precipitated when potassium thiocyanate  $K(NCS)$  is added to a solution of mercuric nitrate. When formed into little balls and burned in the air, the substance leaves a curiously voluminous ash ("Pharaoh's serpents").

**Ammono-Compounds of Mercury.** — When ammonium hydroxide is added to a solution of a mercuric salt, a white substance, of a type which we have not previously encountered, is thrown down. Mercuric chloride gives  $Hg(NH_2)Cl$ , commonly called "infusible white precipitate," or **ammono-basic mercuric chloride**.



The action is similar to an hydrolysis which gives a basic salt:  $HgCl_2 + H.OH \rightarrow Hg(OH)Cl + HCl$ , excepting that ammonia  $H.NH_2$  plays the part of the water. Water gives aquo-basic salts. When liquid ammonia is the solvent, ammono-basic salts are produced. In a few cases, as here, an ammono-basic salt is obtained even when water is present. The study of reactions in liquid ammonia solutions by E. C. Franklin has led to the discovery of a large number of new and most interesting substances.

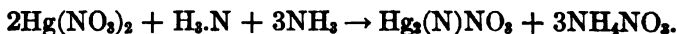
The addition of ammonium hydroxide to a solution of potassium

mercuri-iodide  $K_2HgI_4$  gives rise to a compound of the same type, ammonio-basic mercuric iodide  $Hg_2NI \cdot H_2O$ , which appears as a brown precipitate:



A solution of potassium mercuri-iodide containing potassium hydroxide, **Nessler's reagent**, becomes distinctly yellow with traces of ammonia, and brown with larger amounts, and is, therefore, a valuable reagent for detecting traces of this base.

Mercuric nitrate  $Hg(NO_3)_2$  and ammonium hydroxide give an insoluble **ammonio-basic mercuric nitrate**,  $Hg=N-HgNO_3$  which is more basic than the ammonio-basic chloride:



When calomel is treated with ammonium hydroxide, it turns into a black, insoluble body. This is a mixture of free mercury, to which it owes its dark color, and "infusible white precipitate,"  $Hg + Hg(NH_2)Cl$ . To this reaction calomel owes its name (Gk. *καλόμελος*, beautiful black). Mercurous nitrate gives a black, insoluble mixture,  $2Hg + Hg_2(N)NO_3$ .

Calomel, when *dry*, absorbs ammonia gas, forming a molecular compound of the common type  $HgCl \cdot NH_3$ . This substance loses the ammonia again when the pressure is reduced. The other compounds described above, on the other hand, do not contain nitrogen and hydrogen in the proportions necessary to form ammonia and are stable. Hence they are necessarily to be regarded as belonging to a different type.

**Analytical Reactions of Mercury Compounds.**—The two ionic forms of the element, mercurous-ion  $Hg^+$  and mercuric-ion  $Hg^{++}$ , are both colorless. Their chemical behavior is entirely different. Both give the black sulphide  $HgS$ , which does not interact with acids and other solvents of mercury salts. Mercurous-ion gives the insoluble, white chloride, the black oxide, and a black mixture with ammonium hydroxide. Mercuric-ion gives a soluble chloride, a yellow, insoluble oxide, and a white precipitate with ammonium hydroxide. The behavior with stannous chloride (p. 778) is characteristic. With potassium iodide the two ions behave differently (p. 778). The more active metals displace mercury from all compounds. Copper is used as the displacing metal, in testing for  $Hg^+$  or  $Hg^{++}$ , because the silvery mercury is easily seen on its surface.

Salts of mercury are volatile. When heated in a tube with sodium carbonate, they give a sublimate of metallic mercury.

### THE RECOGNITION OF CATIONS IN QUALITATIVE ANALYSIS

"Wet-way" analysis consists in recognizing the various positive and negative ions present in a solution (p. 385). It was stated that the sulphides might be divided into three classes according to their behavior towards water and acids (pp. 421, 774). Now these differences in behavior furnish us with a basis for distinguishing the cations present in a solution. Since the properties of many sulphides and other compounds of the metals have been studied in recent chapters, it is now possible to make a more complete statement.

The following plan, taken in conjunction with the statements in the context, shows how a single cation may be identified, and how, when several cations are present, a separation preparatory to identification may be effected. What will be said applies only to the case of a *solution* containing salts like the chlorides, nitrates, or sulphates of one or more cations, and leaves the oxalates, phosphates, cyanides, and some other salts, out of consideration.

**Group 1.** — It is usual to add, first, hydrochloric acid, to find out whether cations giving insoluble chlorides are present. Argentie, mercurous, and plumbic salts give the white  $\text{AgCl}$ ,  $\text{HgCl}_2$ , and  $\text{PbCl}_2$ , respectively. (For the further recognition of each, see p. 757.) Filtration eliminates the precipitate, if there is any.

**Group 2.** — A free, active acid being now present, hydrogen sulphide is led into the solution. The sulphides insoluble in active acids, namely,  $\text{HgS}$ ,  $\text{CuS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CdS}$ ,  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}$ , are therefore thrown down. The first four are black or brown, the next two are yellow, and the last two are orange and brown respectively. A dark-colored substance will naturally obscure one of lighter color, if more than one is present. If too much acid is used, the precipitation of several of the sulphides will be incomplete (p. 774); if too little, zinc sulphide may come down (p. 772). Filtration again eliminates the precipitate.

This group is easily subdivided. Any or all of the last three sulphides will pass into solution when warmed with yellow ammonium sulphide, for they give *soluble* complex sulphides similar to potassium sulphaurate (p. 760). The first five sulphides, or any of them, will be unaffected. On the other hand, these five sulphides, with the exception of  $\text{HgS}$ , will interact with hot nitric acid (p. 774). Other reac-

tions described in the context are then used to distinguish between, or, if there is a mixture, to separate, the members of the sub-groups.

**Group 3.** — The solution (filtrate) is now neutralized with ammonium hydroxide, and **ammonium sulphide** is added. Some **ammonium chloride** is also used, to prevent the precipitation of magnesium hydroxide (p. 766), which, in any event, would be incomplete. The sulphides which are insoluble in water, and are not hydrolyzed by it, now appear. They are **FeS**, **CoS**, **NiS**, all black, **MnS** and **ZnS**, which are pink and white, respectively. There are precipitated also the hydroxides of chromium and of aluminium, **Cr(OH)<sub>3</sub>**, and **Al(OH)<sub>3</sub>**, because their sulphides are hydrolyzed by water, and the hydroxides are formed by the hydroxide-ion in the ammonium sulphide solution (cf. p. 648). They are too insoluble to behave like magnesium hydroxide (p. 766) by dissolving in salts of ammonium. They also form no complex metal-ammonia ions, as does zinc (p. 771). The sulphides of nickel and cobalt resemble the sulphide of zinc in being precipitated by hydrogen sulphide when acetic acid is the only acid present. The other sulphides interact even with acetic acid (p. 774).

Another plan is to oxidize the iron, if present, and use ammonium chloride and ammonium hydroxide instead of ammonium sulphide. The hydroxides of the trivalent elements, **Fe(OH)<sub>3</sub>**, **Cr(OH)<sub>3</sub>**, **Al(OH)<sub>3</sub>**, can be precipitated by excess of ammonium hydroxide, even when salts of ammonium are present. Those of the bivalent metals, **Mn(OH)<sub>2</sub>**, **Fe(OH)<sub>2</sub>**, **Zn(OH)<sub>2</sub>**, **Ni(OH)<sub>2</sub>**, **Co(OH)<sub>2</sub>**, resemble magnesium hydroxide (p. 766), and, of these, the last three resemble *also* zinc hydroxide (p. 771), and so cannot be precipitated. After filtration, ammonium sulphide now throws down the sulphides of the five bivalent metals (for a third plan, see Chemical relations of aluminium).

**Group 4.** — After filtration from members of the iron group, if any were present, **ammonium carbonate** is added, and precipitates the remaining metals whose carbonates are insoluble, **BaCO<sub>3</sub>**, **SrCO<sub>3</sub>**, **CaCO<sub>3</sub>**, with the exception of magnesium (p. 767).

By addition of **ammonium phosphate** to a portion of the filtrate, magnesium, if present, now comes out in the form **NH<sub>4</sub>MgPO<sub>4</sub>**. There remain in solution only salts of **potassium**, **sodium**, and **ammonium**. Since only ammonium compounds, and other substances which can be volatilized have been added, evaporation and ignition of the residue leaves the salts of the two metals. If no other metallic elements have been shown to be present, it saves time to

examine a fresh portion of the original material. Salts of ammonium must also be sought in a fresh sample by the usual test (p. 681).

The following simple compounds are soluble, but are so little ionized that their solutions do not show all the reactions of both of the ions:  $\text{NH}_4\text{OH}$ ,  $\text{H}_2\text{S}$ ,  $\text{HNC}$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HgCl}_2$ ,  $\text{Hg}(\text{CN})_2$ ,  $\text{Fe}(\text{NCS})_3$ ,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ . With a number of others, for example  $\text{CdI}_2$ , the actions are incomplete for the same reason. Complex compounds, as we have seen, give complex ions, and these ions are usually so little resolved into simpler ions that the latter cannot be discovered by all the usual tests. Thus:  $\text{K.Ag}(\text{CN})_2$  gives  $\text{K}^+$  and  $\text{Ag}(\text{CN})_2^-$ , but very little  $\text{Ag}^+$  and  $\text{CN}^-$  (p. 752);  $\text{Cu}(\text{NH}_3)_2\text{Cl}_2$  gives much  $\text{Cu}(\text{NH}_3)_2^{++}$ , and  $\text{Cl}^-$  but very little  $\text{Cu}^{++}$ . The individual cases are described in the context.

**Exercises.** — 1. What is the numerical value, (a) of the solubility product of magnesium hydroxide, (b) of the concentration of hydroxide-ion given by it and by normal ammonium hydroxide, respectively ('Table')? Will normal concentration of ammonium chloride suffice to reduce the latter below the former?

2. Why should we, perhaps, expect ammonium sulphide solution to precipitate magnesium hydroxide, and why does it not do so?

3. What volume of air is required to oxidize one formula-weight of zinc sulphide to  $\text{ZnO}$  and  $\text{SO}_2$ , and what volume of sulphur dioxide is produced? Is the product more or less diluted with nitrogen than when pure sulphur is burned, and by how much?

4. Make equations showing, (a) the effect of heating zinc chloride with cobalt nitrate  $\text{Co}(\text{NO}_3)_2$  in the Bunsen flame (p. 771), (b) the action of hydrogen sulphide on sodium zincate, (c) the actions of concentrated nitric acid and of concentrated sulphuric acid on mercury.

5. What is the distinction between a solid isomorphous mixture of two salts and a double salt?

6. What kind of salts might take the place of sodium acetate in the precipitation of zinc sulphide (p. 772)? Give examples.

7. Compare the amalgamation of a gold-leaf by mercury vapor with the phenomenon of deliquescence (p. 776).

8. If the scheme for the recognition of cations (p. 783) were applied to solutions prepared from materials containing, (a) calcium oxalate and, (b) potassium argenticyanide, at what stage and how would the presence of each of these substances affect the normal order?

9. Why do none of the salts of the elements in this family give recognizable effects with the borax bead?

## CHAPTER XXXVIII

### ELECTROMOTIVE CHEMISTRY

We have seen that many chemical changes are accompanied by a liberation of energy. If no special arrangement is made, the energy is always liberated in the form of heat, light, and mechanical energy. In changes involving ionogens, however, the energy can be secured in the form of electricity. Most changes between ionogens, including oxidations, may be adapted so as to deliver this form of energy. It need hardly be added that, since the transformation of chemically equivalent amounts of different sets of substances produces very different quantities of heat, so it produces also correspondingly different amounts of electrical energy. Thus the original free internal energy may, theoretically, be measured by either method. In practice, however, the thermochemical plan fails entirely in many cases (*cf.* pp. 35, 691), and the electrical is, as we shall see, often much more instructive. The study of what, to parody the phraseology of thermochemistry, we might call exoelectrical actions, thus resolves itself into constructing experimental battery-cells involving all kinds of chemical changes, and studying the electric currents which are *set in motion* by the progress of the changes. We have therefore named this branch of the science **electromotive chemistry**.

In addition to its significance theoretically, for the purpose of measuring chemical affinity in ionic actions, electromotive chemistry has recently acquired great commercial importance because of the rapid multiplication of electro-chemical industries. It is true that the majority of the actions used in these industries are electrolytic (endelectrical), and that this sort of change is the precise inverse of the other, since in it electricity is consumed instead of being set in motion, but it is also true that neither variety can be understood without a study of both.

**Factors and Units of Electrical Energy.** — On account of the close relation between electromotive chemistry and electrolysis, parts of the former subject were anticipated when the latter was discussed (pp. 357-361). These pages should now be re-read attentively. In

particular, it must be recalled that a quantity of electrical energy is expressed by two factors. One is called the quantity of electricity, and is measured in coulombs. The other is called the electromotive force in the case of a current, or, when a current is not flowing or is not being considered, the difference in potential, and is expressed in volts. Just as in electrolysis chemically equivalent quantities of elements or ions, in being liberated from solutions of different substances, use up equal quantities of electricity (Faraday's law, p. 350), so in a battery-cell the interaction of chemically equivalent amounts of different sets of substances produces equal quantities of electricity (p. 353). Likewise, just as in the former case different amounts of electrical energy (p. 359), and therefore different electromotive forces, are required to produce in different solutions equivalent amounts of chemical change (p. 216), so in the latter case different amounts of electrical energy are generated by the complete interaction of chemical equivalents of different sets of substances, and therefore diverse differences in potential are created and currents of different electromotive force are produced. The electrical energy used in the former case or produced in the latter is expressed by the product of the factors:

$$\begin{aligned} \text{No. of coulombs} \times \text{No. of volts} \\ = \text{Quant. of elect. energy (in joules, p. 34).} \end{aligned}$$

If we consider the time occupied by either process, and wish to express the rate at which the energy is consumed or produced, we regard 1 coulomb per second (1 ampere) as the unit. Hence:

$$\text{No. of amperes} \times \text{No. of volts} = \text{Joules per sec.} = \text{Watts.}$$

The erg (p. 34) is so small as a unit of energy or work, that the joule (= 10,000,000 ergs) and the kilojoule (1000 joules) are more often employed. Similarly, the rate at which the energy is delivered or used (the power) is expressed by the watt (= 10,000,000 ergs per sec.) or the kilowatt (1000 watts). The horsepower is 746 watts.

An illustration will show the meaning of this relation. If a 50-watt incandescent lamp is used on a 110-volt circuit, by substituting these values in the equation we perceive that such a lamp must carry about 0.5 amperes, or one coulomb every two seconds. If, with the same voltage, we wanted a lamp to carry more electricity per second, we should have to reduce the resistance of the lamp, say, by shortening the filament, or using a thicker one. Evidently, the number of such lamps required to consume one horsepower would be



746/50, or between 14 and 15 lamps. Again, to decompose one molecular weight of hydrochloric acid (36.5 g.) 96,540 coulombs (p. 357) are required, and an E.M.F. of at least 1.83 volts (see p. 798). The electrical energy needed is therefore  $96,540 \times 1.83 = 176,670$  joules. If this were to be accomplished by the current from a 110-volt direct-current lighting circuit, passing through a 50-watt lamp in series with the electrolytic cell, the time required ( $x$  seconds) would be given by 50 joules per sec.  $\times x$  secs. = 176,670 joules, where  $x = 3533$  seconds, or about 59 minutes.

The factors of electrical energy (volts and amperes) are easily measured when electricity is produced, and are easily provided according to any specification when electricity is to be used. Hence, it is much easier to study the relations between chemical change and this form of energy than between the same change and the heat or any other form of energy which, under other conditions, it might produce. Electrochemistry is, therefore, in many ways better understood, and easier to handle than are other branches of chemistry involving energy.

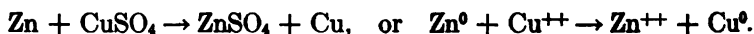
***Some Reactions that can be Used to Furnish Electricity.***

— A few illustrations of the kinds of reactions which can easily be carried out in cells, so as to furnish an electric current instead of heat, may be classified thus:

**Combination cells**, such as one in which zinc (or some other active metal) and bromine are the reacting substances. If zinc be placed in bromine-water (or with pure bromine), we obtain zinc bromide:



**Displacement cells**, such as one with cupric sulphate solution and a metal more active than copper (*e.g.*, Mg, Al, Zn, or Fe), and able to displace (p. 403) this element:



A non-metal may also be displaced:



**Oxidation cells**, such as one in which ferrous chloride  $\text{FeCl}_2$  or stannous chloride  $\text{SnCl}_2$  is oxidized by chlorine-water, giving  $\text{FeCl}_3$  or  $\text{SnCl}_4$ :



**Concentration cells**, or cells in which the same substance in two different concentrations is used.

**The Arrangement of the Cell.**—Every cell has one striking characteristic. If the pairs of substances mentioned in the last section are *placed together*, they interact and *heat* is produced. There is no way to avoid the action, and the liberation of the energy as heat, if the substances come in contact. If, therefore, **all the energy is to be obtained as electrical energy, the substances must be prevented from coming in contact with one another.** Paradoxical as it may seem, it is easily possible to obtain the electricity, and yet fulfill this essential condition. The plan in all cells is to place the one substance in or round one pole, and the other substance in or round the other pole, and to separate the substances by a porous partition, or some equivalent arrangement.

Suppose that it is the first of the above-mentioned actions that is to be used—the action of zinc and bromine. The **active substances are arranged** as follows: The pole on the left (Fig. 149) is metallic zinc. The solution on the right contains the bromine. The porous partition in the center is permeable by migrating ions, but hinders the mere diffusion of the dissolved bromine towards the zinc, and so prevents direct interaction with liberation of heat.

Now, to enable the cell to operate, **inactive, conducting substances must be added** to complete the arrangement. A pole is added on the right, a conducting solution is placed to the left of the partition, and a wire must connect the two

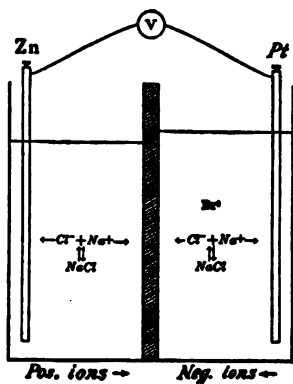


FIG. 149.

poles. The wire may connect the poles through a voltmeter, so that the E.M.F. produced may be measured. Also, since bromine-water is a poor conductor, a well-ionized salt must be present along with the bromine. The substances used for these purposes must be inactive. For example, the pole on the right must be a conductor, but its material must not interact chemically with the bromine or with the salt. A rod of carbon or a platinum wire will serve the purpose. A more active metal, such as copper, could not be used, because it would combine with the bromine. Again, common salt or sodium

nitrate may be mixed with the bromine, because it will not interact with bromine or carbon or platinum. Still again, the solution added on the left must be one which will not act upon the zinc pole, nor upon the solution on the right, which it meets inside the porous partition. Common salt or niter fulfills these conditions. An acid could be used on the right, but not on the left, for it would interact with the zinc. The reader should make a different selection of inactive materials, so as to become familiar with the reasoning involved in the choice in each case.

Note that in each figure, the symbols for the **active substances** are in **black-face type**, the products are in Roman type, and the *inactive* materials are in *italic type*.

**The Operation of the Cell.** — When the cell has been assembled, and the wires have been connected, the following phenomena are observed:

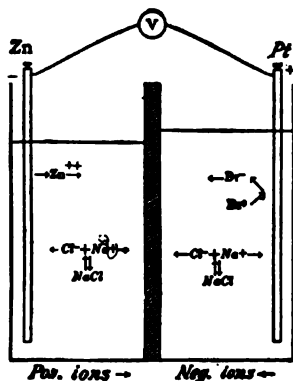


FIG. 150.

1. The zinc begins to form zinc ions,  $\text{Zn} \rightarrow \text{Zn}^{++}$ , an operation which leaves the pole negative (Fig. 150).

2. The bromine molecules nearest their pole touch this pole, become bromide ions,  $\text{Br}_2 \rightarrow 2\text{Br}^-$ , and leave the pole positive.

3. Since one pole is negative and the other positive, a current flows through the wire.

4. The new positive ions ( $\text{Zn}^{++}$ ) round the left pole (anode) attract *all* the negative ions in the cell, and cause them to migrate towards the left so as to keep

all parts of the solution electrically neutral. They also repel all the positive ions.

5. The new negative ions on the right ( $\text{Br}^-$ ) similarly attract *all* the positive ions in the cell, and cause them to drift slowly towards the right pole (cathode). They repel all the negative ions.

6. (Very important.) It will be seen that the zinc and the bromine **become ionized at a distance from one another and do not actually combine**. The slow migration of the  $\text{Zn}^{++}$  and  $\text{Br}^-$  ions will, of course, after some hours or days, bring some of these ions together in or near the partition, and some molecules will be formed. But this operation produces no electrical energy — it only gives out or absorbs

heat (p. 368). It is not an essential part of the operation of the cell. The chemical change which produces the current is the ionization of the two elements, separately. The term combination cell is, therefore, misleading. The cell, as a source of electrical energy, is concerned only with producing two kinds of ions from the elements. True, these ions, if they united, would give the product shown in the equation ( $\text{ZnBr}_2$ ), but the union, if it ever occurred, would be without electrical effect. It is clear that, since there is sodium chloride (or some other ionogen) in all parts of the cell, molecules are ionizing, and ions are combining, continually, throughout the whole system. Thus, on the left some zinc chloride molecules are formed and on the right some sodium bromide molecules, and eventually, near the center, some zinc bromide molecules. But these reactions occur in *every* solution containing ionogens, without giving any current. In a cell, the only reactions which contribute to the current are those taking place at the surfaces of the poles.

**A Displacement Cell.** — In a similar way, a cell using metallic zinc and cupric sulphate solution may be arranged (Fig. 151). The zinc forms one pole, and the cupric sulphate solution *must be placed on the other side of the partition*. For inactive materials, a plate of copper or of some metal below copper in the activity series may be used, and any solution (such as zinc chloride solution) which will interact neither with the zinc nor with the cupric sulphate.

In following the operation of the cell, we may start at either pole. Thus, the zinc gives zinc-ion  $\text{Zn}^0 \rightarrow \text{Zn}^{++} + 2\ominus$ . The wire becomes negatively charged. The cupric-ion is discharged on the other pole  $\text{Cu}^{++} \rightarrow \text{Cu}^0 + 2\oplus$ , rendering it positive. All the positive ions in the cell migrate towards the right pole (cathode). All the negative ions migrate towards the left pole (anode), since positive ions are being formed on the left and are disappearing on the right.

When bromine displaces iodine, the cell may be arranged as in Fig. 152. The iodine liberated dissolves in the potassium iodide solution and, with starch emulsion present, its formation can be detected in a few seconds.

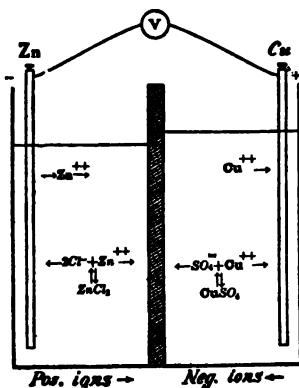


FIG. 151.

**An Oxidation Cell.**—The arrangement whereby stannous-ion  $\text{Sn}^{++}$  is oxidized by chlorine-water to stannic-ion  $\text{Sn}^{++++}$  is shown in Fig. 153. The chlorine  $\text{Cl}^0$  encountering the pole becomes negatively charged, leaving the pole positive. This positive charge is

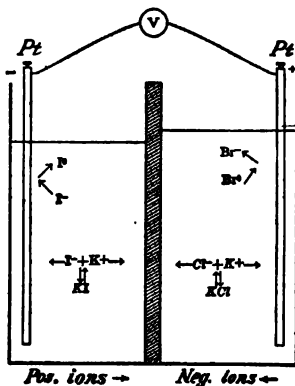


FIG. 152.

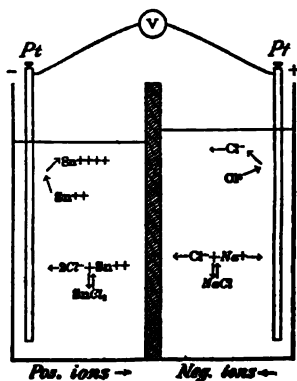


FIG. 153.

shared by the whole conducting wire and, at the other pole, furnishes the positive electricity required to raise the charge of each tin ion from  $\text{Sn}^{++}$  to  $\text{Sn}^{++++}$ . Only the tin ions which *touch* the pole can acquire the charge.

**Facts Concerning all Cells.**—If the wire is disconnected, the progress of the chemical action is stopped, although the difference in potential remains. The charge conferred upon a pole, such as that from the cupric ion (Fig. 151), must be conducted away, before additional charges will be transferred to it.

If a glass partition is substituted for a porous one, the cell ceases to generate electricity. The partition must permit the transmigration of the ions, which is a necessary part of the operation of the cell.

When the circuit is closed, the changes described go on until one of the active materials is exhausted—for example, until all the cupric-ion has been deposited as copper, or until all the zinc has been consumed.

The quantity of electricity produced is 96,540 coulombs for each equivalent weight of the active materials transformed, *e.g.*, for every 65.4/2 g. of zinc consumed. The *rate* at which the elec-

tricity is produced is, in general, greater the larger the area of the poles. The amperage of a *single* cell is, in general, very low.

The E.M.F. of the cell is not changed by altering the size or shape of the poles, or by using more or less of the solutions. It is affected by any change in the *qualities* of the *active* materials, however. Changing the concentration (see p. 794) of the cupric-ion (Fig. 151) or of the bromine-water (Fig. 152) has an immediate effect. So has substituting one active metal for another (see p. 796), as magnesium for zinc (Fig. 150). Even hammering the metal, thus making it denser, has a slight effect.

**Single Potential Differences Produced by the Metals.** — If we reconsider the cells described, we shall see that there are really **two chemical actions in each cell** and that these are to some extent independent. We can leave the zinc (Fig. 150) constant, and change the concentration of the bromine or even substitute chlorine or iodine for the latter. On the other hand, we can leave the bromine-water constant, and exchange the zinc for some other active metal. Thus, the E.M.F. of every cell is really the resultant of two effects. Now, these effects can be measured, separately.

If we place zinc in a solution of zinc chloride, we find that there is at once a difference in potential between the metal and the solution! The metal has an individual tendency to become ionic — a sort of solution pressure\* — and to form a few ions, thus making the liquid positive and the metal negative. In reality, it is the tendency of the atoms of the metal to give up electrons (p. 354), *e.g.*,  $\text{Zn} - 2e = \text{Zn}^{++}$ , which is being observed. On the other hand, the ions have a tendency to deposit themselves, and a few may be deposited (taking up their electrons and becoming neutral), rendering the pole positive and the solution negative. If the former tendency (the tendency to give up electrons) is the stronger of the two (the more active metals), then a difference in potential is produced, with the solution positive. If the latter tendency is the stronger (less active metals) the solution is observed to be negative. Since raising the concentration of the metal-ion will increase the

\* The charge of electricity is apt to interfere with the ready acceptance of this idea. If it is remembered that the ionic form of an element is simply an allotropic modification, with a different amount of available energy, the difficulty disappears. In the ionic allotrope the free energy is sometimes greater (nickel to gold) and sometimes less (potassium to cobalt) than in the free element (see below).

tendency to deposition, and *vice versa*, it is customary to take as the standard solution, for this purpose, one in which the concentration of the metal-ion is normal (*N*). The ions of the foreign salt, if such a salt was introduced at first, need not be considered. In the following table, the sign preceding the number is that of the charge of the *solution*.

POTENTIAL OF *N* SOLUTIONS IN CONTACT WITH METALS  
(E.-M. SERIES)

K	(+2.6)	Fe (Fe <sup>++</sup> )	+0.2	Bi	-0.63?
Na	(+2.4)	Cd	+0.16	Sb	-0.71?
Ba	(+2.6)	Co	+0.05	Hg (Hg <sup>+</sup> )	-0.99
Sr	(+2.5)	Ni	-0.02?	Pd	-1.03?
Ca	(+2.4)	Pb	-0.12	Ag	-1.04
Mg	+1.3	Sn (Sn <sup>++</sup> )	-0.14	Pt	-1.10?
Al	+1.0	H	-0.24	Au	-1.7?
Mn	+0.8	As	-0.53		
Zn	+0.5	Cu (Cu <sup>++</sup> )	-0.58		

Thus, opposite Mg we find +1.3. This means that when a piece of magnesium is placed in a solution of a salt of magnesium, containing normal concentration of Mg<sup>++</sup>, the solution is positively charged (the metal negatively) and the difference in potential is 1.3 volts. With silver in a solution of a salt of silver, containing normal concentration of silver-ion, the solution is negative and the difference in potential is -1.04 volts.

For a hydrogen pole, a piece of palladium saturated with hydrogen at 760 mm. (p. 124) is used. The values for the metals which decompose water with ease cannot be observed, and so calculated values are given in parentheses. An interrogation point indicates that the value is uncertain.

**Calculation of the Potential with Varying Concentrations.**

— These facts enable us to state in more definite terms the formulative hypothesis foreshadowed above. It was first put forward by Nernst.

Every metal has a certain **solution tension**, or pressure, tending to drive it into solution (in ionic form, of course, since it is not soluble otherwise). The value of this pressure becomes rapidly less as we pass through the series from magnesium to gold. If the ions of the same metal are already present, they tend to give up their electrical

charges and deposit themselves upon the metal. These two tendencies oppose one another, just as solution pressure and diffusion pressure oppose one another in the ordinary process of dissolving any substance (p. 186). When the tendency of the ions to deposit themselves is the greater of the two, a very minute excess of deposition over solution occurs, and thus the solution has, as a whole, a negative charge (having lost some positive ions), and the metal has a positive charge (having acquired it from the deposit of a few ions). This is the case with gold and the metals as far up the list as nickel. When, on the other hand, the solution pressure of the metal is the greater of the two, the solution acquires a very slight excess of positive ions, and is, therefore, positively charged when compared with the metal. This is the case from potassium down to cobalt.

The measure of the "tendency of the ions to deposit themselves" is simply the diffusion pressure of the metal-ions. We perceive this to be the case, for, when we take a stronger solution of the salt, and therefore an increased diffusion pressure of the ions, an instant effect is produced. The solution becomes less positive, or more negative, as the case may be. Evidently the solution pressure of each of the metals near to cobalt and nickel is almost exactly balanced by the diffusion pressure of a normal solution of the ions composed of the same metal. This pressure, for a univalent metal, is 22.4 atmospheres (p. 333), and for a bivalent metal 11.2 atmospheres. The metals above nickel have solution pressures higher and higher above this norm; those below cobalt have solution pressures farther and farther below it. The effect of changing the diffusion pressure is independent of the particular substances used, and depends only on the valence. When the concentration of the metal-ion becomes  $10N$ , 0.058 volts must be subtracted (algebraically) from the potential (see above table) of the liquid, if the metal-ion is univalent. If it is  $n$ -valent,  $0.058/n$  must be subtracted. When the solution is  $0.1N$ ,  $0.058/n$  volt must be added; when it is  $0.01N$ ,  $2 \times 0.058/n$  must be added, and so forth. Thus, zinc with decinormal zinc-ion gives  $+0.5 + 0.058/2 = 0.53$  volts, approximately; silver with centinormal silver-ion gives  $-1.04 + (2 \times 0.058) = -0.924$  volts, approximately. And, in general, if  $c$  be the equivalent concentration of the metal-ion in the liquid under consideration, and  $\pi_c$  the electrical potential of that liquid, while  $\pi_N$  is the potential of the liquid containing  $N$  metal-ion,

$$\pi_c = \pi_N + \frac{0.058}{n} \log \frac{1}{c}.$$



**Applications: E.M.F. of a Displacement Cell.**—When, now, a cell with *two* poles and *two* metal-ions is set up, we can tell from the above table what the difference in potential between the two poles will be. We may regard the two systems—the anodic and cathodic—as working against each other. Each metal tends to project its ions into the solution and to generate a positive current in the liquid and a negative one in the wire. If both solutions are normal, or, in general, of equal equivalent concentration, the relative solution pressures of the metals decide the direction of the resultant current, and its magnitude will be the *difference* of the two effects. Thus, the values for the following pairs will be:

$\text{Zn}-\text{Cd}^{++}$ ,  $+0.5 - (+0.16) = +0.34$ , Zinc the negative pole.

$\text{Cd}-\text{Cu}^{++}$ ,  $+0.16 - (-0.58) = +0.74$ , Cadmium the negative pole.

$\text{Zn}-\text{Cu}^{++}$ ,  $+0.5 - (-0.58) = +1.08$ , Zinc the negative pole.

The **Daniell** or **gravity cell** (Fig. 154) represents the last of these three combinations. The copper pole is at the bottom, and the zinc plate is suspended above it. The cell is charged with a dilute solution of sodium chloride, and blue vitriol crystals are thrown in and dissolve. So long as the contents are not disturbed, the solutions require no porous septum to keep them apart. It is true that, when the current is not being used, and the cell is not working, the cupric sulphate diffuses upwards. During the time that the circuit is closed, however, the effects of diffusion are nullified by the migration of the cupric ion away from the zinc and towards the positive pole. The actual E.M.F. of this cell is not exactly that calculated above for normal solutions, because the cupric sulphate is in saturated solution, and the concentration of the zinc-ion varies, starting at zero and increasing as the cell is used. It is, however, a little over 1 volt.

The cell  $\text{Zn}-\text{H}^+$  ( $+0.5 - (-0.24) = 0.74$  volts) works without a septum, provided the direct action of the zinc on the acid is minimized by adequate amalgamation with mercury. It gives a very inconstant electromotive force, however, because the platinum plate used as the cathode becomes covered with bubbles of hydrogen, and so the internal resistance of the cell is greatly increased. The polarization (p. 360) also diminishes the electromotive force. These

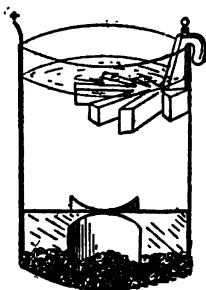


FIG. 154.

difficulties are remedied, and, in fact, a great increase in the E.M.F. of the cell is effected, by surrounding the cathode with an oxidizing agent which shall convert the hydrogen into water. The energy obtainable is thus that of a strong oxidizing agent on zinc, and not merely that of an acid. In the **Bunsen cell** the cathode is a carbon block surrounded by concentrated nitric acid. In the **dichromate battery** it is a carbon block with chromic acid. Each of these cells gives an E.M.F. of 1.9 volts. In the **Leclanché cell** the cathode is a mixture of carbon and manganese dioxide, and the fluid is a solution of ammonium chloride from which the zinc displaces hydrogen. The dioxide, being solid, oxidizes the hydrogen slowly, and the cell can be used for only a few minutes at a time without becoming polarized. The E.M.F. is 1.48 volts. **Dry cells** are of the same nature, but contain a porous solid which holds the liquid by capillary forces (for Accumulators, see under Lead).

A cell is thus an engine for the direct transformation of chemical into electrical energy, just as a steam-engine transforms chemical energy, by several stages, it is true, into mechanical energy. The cell is driven by pressure-differences in the materials in and around the two poles.

The **Weston Standard Cell** contains a pole of mercury in a saturated solution of mercurous sulphate, and cadmium in contact with saturated cadmium sulphate solution. For *normal* solutions, the voltage would be  $+0.16 - (-0.99) = 1.15$  volts. At  $20^\circ$  it is 1.0183 volts.

The **Clark Standard Cell** contains zinc and zinc sulphate solution in place of the cadmium. With *normal* solutions it would give  $+0.5 - (-0.99) = 1.49$  volts. It actually gives 1.434 volts.

**Single Potential Differences for Non-Metallic Ions.** — The corresponding figures for the non-metals are:

$I^-$	-0.78	$Cl^-$	-1.59	$HSO_4^-$	-2.9
$Br^-$	-1.32	$OH^-$	-1.96		
$O=$	-1.36	$SO_4=$	-2.2		

As before, the anode potential is supposed to work against the cathode potential and is subtracted from it. Hence the cell with zinc and bromine-water (p. 789) in presence of normal concentration of the respective ions, gives  $+0.5 - (-1.32) = 1.82$  volts. Similarly, the cell in which bromine displaces iodine (p. 791) gives  $-0.78 - (-1.32) = 0.54$  volts.

**Applications : Electrolysis : Discharging Potentials.**

When a solution of a salt, such as cupric chloride, is electrolyzed copper and chlorine are liberated at the two poles. Now, when the electrolysis has made some progress, if the battery is taken out, and the wires are joined, a current, the **polarization current** flows. Evidently, the copper and chlorine liberated in and round the electrodes have made the arrangement into a copper-chlorine battery cell. Assuming normal concentrations, the E.M.F. of the polarization current is  $-0.58 - (-1.59) = 1.01$  volts. Now the counter-current is in operation during the whole electrolysis. To overcome it, and maintain the electrolysis, evidently an E.M.F. of at least 1.01 volts from the battery is required. This is called the **discharging potential** for cupric chloride.

Again, a tin-chlorine cell produces  $-0.14 - (-1.59) = 1.45$  volts and this E.M.F. will just suffice to electrolyze tin chloride. Similarly, hydrochloric acid will require at least  $-0.24 - (-1.59) = 1.35$  volts, and zinc sulphate  $0.5 - (-2.2) = 2.7$  volts.

Oxygen acids like sulphuric acid show a trace of decomposition at 1.12 volts ( $= -0.24 - (-1.36)$ ), and a noticeable but still small decomposition at 1.72 volts ( $= -0.24 - (-1.96)$ ), due to the  $H^+$  and  $O^=$  and the  $H^+$  and  $OH^-$  respectively. But it is only when the E.M.F. reaches the values for  $H^+$  and  $SO_4^=$ , and  $H^+$  and  $HSO_4^-$ , namely, 1.96 and 2.66 volts, that rapid electrolysis begins. This observation answers, incidentally, the question whether in the so called "electrolysis of water," when dilute sulphuric acid is used, it is the water or the acid that is decomposed. The  $H^+$  and  $OH^-$  decomposition at 1.72 volts is very slight, because of the small concentration of the  $OH^-$ , and a lens is required for its recognition. The more vigorous action resulting from the discharge of  $SO_4^=$  and  $HSO_4^-$  by the use of 2-3 volts is therefore the one invariably used.

In view of the foregoing facts, it is probably most correct to say that when dilute sulphuric acid is electrolyzed, *e.g.*, as a lecture experiment, the oxygen liberated at the anode comes mainly from a secondary interaction of the discharged material of the anions with the water (p. 121). A minute proportion of the oxygen in such an experiment does arise from primary electrolysis of the water, but this effect of the current is in itself too slight to be visible at a distance. When, on the other hand, the solution electrolyzed contains a salt of sodium, and hydrogen is liberated at the cathode, this gas must be regarded as coming chiefly from primary electrolysis of the water. The discharging potential for sodium chloride should be  $+2.4 -$

(-1.59) = 3.99 volts, and with the help of a mercury cathode a sodium amalgam is easily obtained (p. 667). But it will be found that, with platinum electrodes, hydrogen and chlorine are liberated freely from a solution of salt by a current of little more than half the above mentioned E.M.F. The positive electricity is carried in the liquid mainly by the very numerous sodium ions. But, when these ions reach the cathode, the potential difference, being insufficient to discharge the sodium-ion, liberates the hydrogen-ion of the water instead. Thus the accumulating hydroxide-ion of the water, and the sodium-ion arriving by migration, together constitute the sodium hydroxide which is another product of this electrolysis. With high E.M.F. and sufficient current density, sodium-ion is doubtless actually discharged, and in that case a part of the hydrogen liberated is furnished by the interaction of the metal with the water.

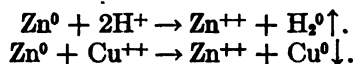
The ordinary chemical behavior of the halogens accords with the order of their potential differences. Bromine displaces iodine, and chlorine displaces both (p. 285). Chlorine, however, does not displace easily perceptible amounts of oxygen from water, because of the small concentration of the  $O^=$  (obtained by secondary ionization of the  $OH^-$ ). The oxygen freely liberated in sunlight comes from the decomposition of the  $HClO$  (p. 223). Fluorine, however, which would probably show a potential difference below that of the much more plentiful  $OH^-$ , displaces oxygen vigorously by discharging this ion.

**Applications: Electrolytic Refining.** — The electrolytic process of refining copper (read p. 747) can now be more easily understood. Both electrodes are made of copper, and the solution contains cupric sulphate. There is, therefore, no difference in potential between the plates, except a very small one, due to the fact that one plate is pure copper and the other impure. Hence a very slight E.M.F., sufficient to overcome the difference just mentioned, and to overcome the friction of the moving ions, is all that is required, and 0.5 volts is sufficient.

As regards the resulting purification, the anode of crude copper, which is being consumed, contains, besides copper, small amounts of less active metals like silver and gold, and of more active metals like zinc. So far as the more active metals are concerned, the cell is like one with zinc and cupric sulphate (p. 791). It would run *by itself*, without any outside current, and would actually generate a current. Hence the active metals become ionic easily, and displace cupric-ion from the solution. The less active metals, on

the other hand, are not required for the transference of the electricity, since a great excess of the more active copper is available. They also require a larger E.M.F. for their ionization than does copper. Hence, they remain as metals, and drop to the bottom of the cell (sludge) as the anode of crude copper wears away.

**Applications: Couples.** — The fact that metallic zinc will displace hydrogen-ion from an acid, or cupric-ion from cupric sulphate solution can now be explained. The more active metals are the ones which have the greatest tendencies to become ionic. Each will deprive the ions of a metal below it in the list of their electric charges:



Now we have noted the facts (pp. 119, 769) that contact with a platinum wire, or the presence of impurities (other metals) in the zinc, will hasten its action. Pieces of two metals in contact with one another constitute a **couple**. With zinc and platinum in an acid, a current is set up, like that of a short circuited cell. The zinc becomes negative, the platinum positive, and the hydrogen is *liberated upon the platinum*. This facilitates the action because, when the platinum is absent, and the hydrogen gas, in bubbles, is liberated on the surface of the zinc, this surface is only partly in contact with the acid ( $\text{H}^+$ ), and so the liberation of the hydrogen is slower.

**Galvanized iron** is also a couple. When rain (dilute carbonic acid) falls upon it, the zinc, being the more active metal (p. 794), is the anode and tends to become ionized (forming the carbonate). The iron is the cathode and is not affected. The carbonate, however, forms a closely adhering coating on the zinc, and so but little of this metal is actually consumed, and the material is therefore durable. On the other hand, a sheet of iron, without the zinc coating, gives ferrous carbonate which is easily oxidized to ferric hydroxide (a base too weak to give a carbonate). This forms a brittle, porous layer which does not mechanically protect the surface from further action, and so the iron is finally all oxidized. **Tin-plate** (tin on iron, a couple) is not attacked so long as the layer of tin is nowhere broken. But damaged tin-plate rusts rapidly. There, the iron is the more active metal (p. 794) and forms carbonate and then hydroxide continuously, while the tin remains unaffected.

**Rusting.** — It seems to be generally overlooked that *two* factors are concerned in determining **extent to which the rusting or tarnishing of a metal will proceed**. Other things being equal, it should depend upon the order of activity of the metals, since it is a question of action upon surface moisture containing carbonic acid, with atmospheric oxygen as an assistant when the metal does not liberate elementary hydrogen (*e.g.*, Copper, p. 745). But this applies only to the initiation of the action. The physical qualities of the product then determine whether the rusting shall be superficial or shall go deeper. Magnesium (p. 765) and iron (p. 800) give carbonates, and the latter eventually a brittle, scaly hydrated oxide. In both cases, the porous product harbors moisture and thus promotes further rusting. Aluminium is more active than is iron, but the horny, gelatinous, closely adherent hydroxide first formed protects the surface from further action. The same is true of zinc and tin.

**Concentration Cells.** — If two rods of a metal (*e.g.*, tin) are placed together in the same solution of a salt of the metal (*e.g.*, stannous chloride  $\text{SnCl}_2$ ), there is no difference in potential, because the state of both poles is in all respects the same, and no current flows when they are connected by a wire. The two poles and their solutions are here alike and  $-0.14 - (-0.14) = 0$ . But if the

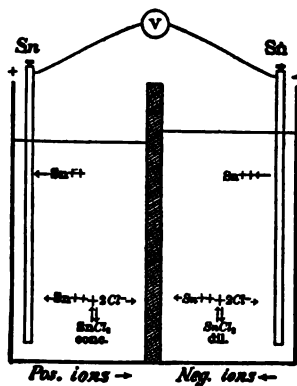


FIG. 155.



FIG. 156.

solution round one pole is diluted to  $N/10$  concentration, the potential at that pole becomes at once  $-0.14 + 0.058/2 = -0.11$  volts, approximately, and a current is set up (Fig. 155). The tendencies of the metallic tin to form ions are equal, but the pressures of the stannous ions are different, and so, when the circuit is closed, stannous ions are discharged on the tin pole in the more concentrated

solution, forming long crystals of tin, and tin in equal amount from the pole in the dilute solution becomes ionic.

Figure 156 shows the simplest arrangement, where the more concentrated, denser liquid is below, and one rod of tin, passing through both layers, furnishes at once the two poles and the connection. The chloride-ion migrates through the solution, in a direction opposite to that taken by the tin ions, and thus passes upwards into the dilute solution to balance the fresh tin ions that are continuously formed. All change ceases when the concentrations have become equalized.

The concentration cell is instructive because it shows that the order of the metals in the electromotive series is not determined by the metal alone, but also by the concentration of the solution. The order of the metals in the electromotive series is therefore subject to variation. An extreme case of this occurred in a recent chapter. Zinc displaces copper from a solution of a cupric (or cuprous) salt, and any but a prodigiously dilute solution will show the effect. But a solution containing cuprocyanide-ion  $\text{Cu}(\text{CN})_2^-$  has precisely this very minute concentration of copper ions which will turn the scale. Hence, zinc will not displace copper from this solution (p. 744). On the contrary, copper will displace zinc from a solution of a salt of the latter containing excess of potassium cyanide, and therefore the complex salt  $\text{K}_2\text{Zn}(\text{CN})_6$ .

The law which formulates the relation between the two concentrations and the E.M.F. produced being known (p. 795), it is possible to use the concentration cell for measuring solubilities of insoluble salts. Thus, we cannot easily measure the solubility of silver chloride by the ordinary method (p. 180), because evaporation of the solution may leave a larger mass of impurities, derived from solution of the glass, than of dissolved silver chloride. Hence, we use two poles of silver, place one in normal silver nitrate solution and the other in saturated silver chloride solution (with excess of the solid), measure the difference in potential, and calculate the ratio of the concentrations of silver-ion in the two solutions. The absolute value of that in the silver nitrate solution is known, and so the absolute value of the  $\text{Ag}^+$  concentration in the silver chloride solution can be found. Since silver chloride is a salt (p. 369), it is very highly ionized in so dilute a solution, and the molecular concentration of silver-ion is practically equal to the total molecular concentration of silver, and therefore of silver chloride in the liquid.

**The Factors of Energy.** — We have seen that the amount of a given supply of electrical energy is described by two factors, the E.M.F. and the quantity of electricity, and that the weight of material, which, by its influence, undergoes a given chemical change, is proportional solely to this second factor. On the other hand, the question whether the supply of energy can *initiate the change at all* depends on the magnitude of the first factor alone (p. 798). The total amount of available energy does not influence the result if the E.M.F. is not above a certain minimum, which differs from case to case. Now the same is true of other kinds of energy. The quantity of each may be expressed as the product of an **intensity** factor and a **capacity** factor. The magnitude of the former determines whether the energy can be transferred or transformed or not. Heat energy, no matter how much of it is at hand, can neither flow nor be transformed into work unless the source is at a higher **temperature** (intensity factor) than the surroundings. A head of water will do work only when it is connected with a receptacle at a lower level. It is the **pressure** of the water that determines its availability. The E.M.F. is the intensity factor of electrical energy.

Now we may presume that chemical energy can also be expressed by two factors. One of these, the capacity factor, must be proportional to the quantity of material, in other words, to the number of chemical equivalents. The other is the **chemical potential** (intensity factor). A chemical change which does not take place on a small scale will not take place when more material is used, provided the relative amounts of the interacting substances and the conditions remain unchanged.\* We have, in fact, been assuming all along that this, the capacity factor, is not the most significant one. But we have devoted ourselves to noting such things as these: that chlorine will displace bromine, and therefore has the higher potential of chemical energy; that magnesium reduces sand, while hydrogen does not, and that magnesium is therefore a more active reducing agent; and that hypochlorous acid will oxidize indigo, while free oxygen will not, and is therefore a more powerful oxidizing agent. When we were comparing degrees of **activity**, therefore, we were really trying to describe the relative potential of the chemical energy in all sorts of substances. At present, the state of the science permits this to be done in most cases in a rough fashion only.

\* Change in concentration, a condition, however, does affect activity, and therefore modifies the chemical potential.



**Applications: Measurement of Affinity.**—Since the capacity factor of chemical energy is proportional to the number of equivalent weights transformed, and the capacity factor of electrical energy is proportional to the same thing (Faraday's law), it follows that the intensity factor of the chemical energy (the chemical potential) in a given substance undergoing a given change, must be proportional to the corresponding factor (the E.M.F.) of the electrical energy produced when the same change takes place in a suitable cell. Thus the activities of the metals, expressed in volts (p. 794), are accurate figures for the relative affinities of the metals, so far at least as ionic actions are concerned. In point of fact, they express also the approximate affinities of the metals in other actions (p. 404) as well. Again, by using different oxidizing agents in place of the chlorine-water (p. 792) and noting the differences in potential, we can obtain numbers representing the relative activities of various oxidizing agents towards oxidizable ions. The potential differences described above are therefore often much more significant than are the results of thermochemical measurements, for the latter attempt to give only the gross quantity of chemical energy (in terms of the equivalent amount of heat energy), and not the values of the factors. The potential differences come nearer, therefore, to giving us absolute values for chemical activity than do any other data we possess.

As we have noted before (p. 100), in spite of the enormous range of temperature at our disposal, extending to a point far above 2500° in the electric furnace, there are many substances for whose decomposition a sufficient potential of heat energy is not available. On the other hand, amongst substances that are capable of furnishing an electrolyte, when dissolved in a suitable solvent or when fused, there are few that are not decomposable by a current with an E.M.F. of less than 10 volts. Hence even the elements which give the most stable compounds and are the most difficult to isolate, such as calcium and aluminium, are liberated by electrical methods with extreme ease.

The idea that every kind of energy is described by two factors, which play different rôles, serves to clarify our thoughts about many things. For example, one author says: "Valence is a form of chemical energy." Now valence is the number of equivalents contained in the atomic weight. It is the value of the capacity factor, only, of the energy in one atomic weight. It is not a form of energy, because it takes no account of the intensity factor. Again, the same author says: "Chemical energy is identical with chemical affinity." Yet the affinity between a single atom of sodium and a single atom of chlorine is the same as that between 23 kilograms of the one and 35.46 kilograms of the other, although there is only a

trace of energy produced by union of the two atoms and a relatively immense amount by the union of the larger quantities. Chemical affinity is the intensity factor of chemical energy only, and we must have also the amount of material (capacity factor) before the whole statement conveys any information about energy. Fourteen is a factor. If the other factor is pins, the amount of material is specified, but very small. If the other factor is elephants, then the amount of matter is much greater. Fourteen by itself conveys no meaning.

**Methods of Measuring Chemical Activity.** — The following is a summary of the methods of measuring chemical activity.

The **thermochemical method** (p. 98) can be used in every chemical change. But the heats of reaction represent the free energy, and therefore the affinity, only when the heat capacity of the products is equal to that of the factors and no changes in concentration arise.

For measuring the **activity of acids** in dilute solution, several methods have been mentioned: The speed of interaction of different acids with the same metal (p. 128); the acceleration of the speed of hydrolysis of ethyl acetate (p. 617-8) and of cane-sugar (p. 606) by different acids; the amounts of insoluble salts, such as calcium oxalate (p. 713), or zinc sulphide, which, when the system has reached equilibrium, are found to have been decomposed by different acids under like conditions; the relative extents of the hydrolysis of salts of different weak acids (p. 648); the electrical conductivity (p. 365) and the freezing- and boiling-points of solutions of acids (pp. 336, 337). These last measure by physical methods the same thing that the others determine by chemical means, namely, the tendency to ionization on which the activity of acids depends (p. 369. See also p. 392).

For measuring the **activity of bases** we have: The relative speeds of saponification of esters by different bases (p. 618); the relative extents of the hydrolysis of salts of different weak bases (p. 399); the conductivity and the freezing- and boiling-point methods, which measure by physical means the tendency to ionization.

For measuring the **relative activities of metals and of non-metals** we have: The single potential differences (pp. 794, 797); and, for the former, the speeds of interaction of different metals with the same acid (p. 128).

For measuring the **relative activity in non-reversible actions** we have: The speed with which the actions take place under like conditions (p. 294).

For measuring the **relative activities of the opposed actions in reversible changes**, we have: The concentrations of the materials remaining when equilibrium has been reached (p. 298). The relative

activities in different reversible changes may also be ascertained by comparing the concentrations in one, at equilibrium, with those in another (cf. p. 299).

For measuring the relative activities of oxidising and reducing agents, we have: The potential differences in cells arranged after the manner of the Bunsen and Leclanché cells (p. 792).

If we consider the whole mass of phenomena, it must be admitted that the scientific study of the quantities of material has reached a far higher level of exactness, and has very much more nearly enveloped the whole field covered by the science, than has the study of relative activity. Yet it is evident that within the past few years substantial advances have been made in this direction also.

**Exercises.** — 1. Make diagrams of the following cells, choosing with care suitable inactive substances to complete the arrangement: (a) chlorine-water and aluminium; (b) chlorine-water and ferrous chloride; (c) zinc and dilute sulphuric acid; (e) chlorine-water and potassium bromide.

2. Calculate the E.M.F. of each of the cells in Ex. 1, assuming normal solutions to be present.

3. What will be the discharging potentials of solutions of the following substances, assuming *N* concentrations of the ions: (a) manganous chloride; (b) hydrogen iodide; (c) ferrous bromide; (e) sodium chloride (hydrogen is liberated)?

4. What weight of zinc must be ionized every hour in a cell in order to produce a current of 5 amperes strength? For how long would 500 g. of zinc serve to maintain this current?

5. What will be the E.M.F. of a concentration cell in which the poles are of lead and the lead-ion is one hundred times more concentrated round one pole than round the other?

6. What weight of aluminium must become ionized every hour in a cell in order that a current of five amperes strength may be produced? What would be the E.M.F. of the current if an acid with normal concentration of hydrogen-ion surrounded the cathode and a solution of normal aluminium-ion the anode? How would this E.M.F. be affected if the aluminium-ion were only one-hundredth normal?

## CHAPTER XXXIX

### ALUMINIUM AND THE METALLIC ELEMENTS OF THE EARTHS

THE fourth column of the periodic table contains boron and aluminium along with a number of rare elements. The chief members of the family are: boron (B, at. wt. 11), aluminium (Al, at. wt. 27.1), gallium (Ga, at. wt. 69.9), indium (In, at. wt. 114.8), thallium (Tl, at. wt. 204), all on the right side of the column; and scandium (Sc, at. wt. 44.1), yttrium (Yt, at. wt. 88.7), lanthanum (La, at. wt. 139), on the left side. These elements are all trivalent.

**The Rare Elements of this Family.** — The oxide and hydroxide of boron are acidic (p. 637). Those of aluminium  $\text{Al}(\text{OH})_3$ , gallium  $\text{Ga}(\text{OH})_3$ , indium  $\text{In}(\text{OH})_3$ , and thallium  $\text{TlO.OH}$  are basic, but behave also as acids towards strong bases.

**Gallium** and **indium** occur occasionally in zinc-blende, and were discovered by the use of the spectroscope. The former takes its name from the country (France) in which the discovery was made, and the latter from two blue lines shown by its spectrum. Indium gives a complete series of compounds in which it is trivalent, and the chlorides  $\text{InCl}$  and  $\text{InCl}_3$  are also known.

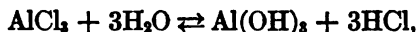
**Thallium** is found in some specimens of pyrite and blende. It was discovered by Crookes, by means of the spectroscope, in the seleniferous deposit from the flues of a sulphuric acid factory. It received its name from the prominent green line in its spectrum (Gk. *θαλλός*, a green twig). It gives two complete series of compounds. In those in which it is trivalent (thallic salts), it resembles aluminium (*q.v.*). Thus, the salts of this series are more or less hydrolyzed by water. Univalent thallium recalls both sodium and silver. Thallous hydroxide  $\text{TlOH}$  is soluble, and gives a strongly alkaline solution, but the chloride is insoluble in cold water. The solutions of the thallous salts are neutral. The metal is displaced from its salts by zinc.

Of the elements on the left side of the column, **scandium**, whose existence and properties were predicted by Mendelejeff (p. 465), is the best known. The metals of the **rare earths**, of which it is one, are found in rare minerals such as euxenite, gadolinite, orthite, and mona-

zite, which occur in Sweden, Greenland, and the United States. **Cerium** (Ce, at. wt. 140.25) **neodymium** (Nd, at. wt. 144.3), and **praseodymium** (Pr, at. wt. 140.9) occur along with **lanthanum** in cerite, a silicate of these four elements. These four are included amongst the metals of the rare earths. The compounds of many of these rare elements behave so much alike that separation is difficult. It is certain, however, that there are several with atomic weights near to that of lanthanum for which accommodation cannot easily be found in the periodic table. Ostwald has compared them to a group of minor planets such as, in the solar system, takes the place of one large planet.

#### ALUMINIUM AL

*The Chemical Relations of the Element.*—Aluminium is trivalent exclusively. Its hydroxide, like that of zinc (p. 771), is **amphoteric**, that is to say, it is feebly acidic as well as basic, and hence the metal forms two sets of compounds of the types  $\text{Na}_3\text{AlO}_3$  and  $\text{Al}_2(\text{SO}_4)_3$ . The salts of both series are more or less hydrolyzed by water, the former very conspicuously so. It is worth noting that the hydroxides of the trivalent metals, or metals in the trivalent condition, such as  $\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$ , are all distinctly less basic than are those of the bivalent metals such as  $\text{Zn}(\text{OH})_2$ ,  $\text{Cd}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_2$ ,  $\text{Mn}(\text{OH})_2$ . This fact is **used in analysis** (cf. also p. 784) in separating the two sets. When a solution of the chlorides is shaken with precipitated barium carbonate, the free acid from the more highly hydrolyzed salts of  $\text{Al}^{+++}$ ,  $\text{Cr}^{+++}$ , and  $\text{Fe}^{+++}$  interacts with this substance, the hydrolysis is promoted:



and eventually the hydroxides  $\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ , and  $\text{Fe}(\text{OH})_3$  are completely precipitated. The chlorides of the bivalent metals remain in the solution. Aluminium does not enter into complex anions or cations. In this it differs from zinc and resembles magnesium. It is too feebly base-forming to give salts like the carbonate or sulphite, because hydrolysis causes precipitation of the hydroxide (p. 656, see p. 814).

*Occurrence.*—Aluminium is found very plentifully in combination, coming next to oxygen and silicon in this respect. The feldspars (such as  $\text{KAlSi}_3\text{O}_8$ ), the micas (such as  $\text{KAlSi}_3\text{O}_{10}$ ), and kaolin (clay)  $\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$  are the commonest minerals containing it. Since

the soil has been formed largely by the weathering of minerals like the feldspars, clay and other products of the decomposition of such minerals constitute a large part of it. Garnets, which are found in metamorphic rocks, are mainly an orthosilicate of calcium and aluminium  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ . Turquoise is a hydrated phosphate  $\text{Al}_2(\text{OH})_2\text{PO}_4 \cdot \text{H}_2\text{O}$ , and cryolite a double fluoride  $3\text{NaF} \cdot \text{AlF}_3$ . Various forms of the oxide and hydroxide are also found.

**Preparation and Physical Properties.**—The metal is now made on a large scale by electrolysis of the oxide  $\text{Al}_2\text{O}_3$  dissolved in a bath of molten cryolite (m.-p.  $1000^\circ$ ), a process invented by C. M. Hall (1886). The operation is conducted in cells ( $5 \times 3$  feet, or larger), the carbon linings of which form the cathodes (Fig. 157).

The anodes are rods of carbon, which combine with the oxygen as it is liberated. The metal (m.-p.  $659^\circ$ ) sinks to the bottom of the cell and is drawn off periodically, while fresh portions of the oxide are added from time to time. The oxide is made from bauxite (see below), and must be free from oxide of iron and other impurities, as the metal cannot be purified commercially. A current density of 5 amperes per sq. cm. of cathode

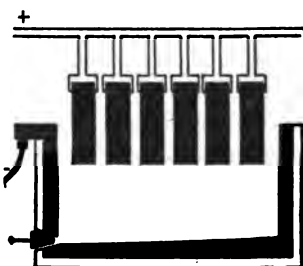


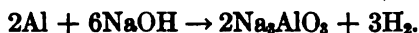
FIG. 157.

area and an E.M.F. of 5–6 volts maintain the temperature of the molten materials, and cause the decomposition. In 1866 aluminium cost \$250–750 (£50–150) per kilogram. In 1883 the whole production was about 40 kilos. In 1913 the United States alone consumed 35 million kilos, costing about 50 cents (2/–) per kilo.

The metal melts at  $658.5^\circ$ , but is not mobile enough to make castings. It is exceedingly light (sp. gr. 2.6), and in tensile strength excels the other metals, with the exception of iron and copper. It is malleable, and the foil is taking the place of tin-foil for wrapping foods. It has a silvery luster, and tarnishes very slightly, the tough, *firmly adhering* film of hydrated oxide first formed protecting its surface. Although, comparing cross-sections, it is not so good a conductor of electricity as is copper, yet *weight for weight* it conducts better. It is difficult to work on the lathe or to polish, because it sticks to the tools, but the alloy with magnesium (about 2 per cent), called **magnalium**, has admirable qualities in these respects. **Aluminium bronze** (5–12 per cent aluminium) is easily fusible, has a magnificent

golden luster, and possesses mechanical and chemical resistance exceeding that of any other bronze. The metal and its alloys are used for making cameras, opera-glasses, cooking utensils, and other articles requiring lightness and strength, such as air-ships, automobile and bicycle parts, and brewing vats, as well as for the transmission of electric currents. The powdered metal, mixed with oil, is used in making a silvery paint.

**Chemical Properties.**—The metal displaces hydrogen from hydrochloric acid very easily. In sulphuric and nitric acid, however, it receives a coating of the hydroxide, formed by hydrolysis of the salt, and the action is slow in the former case, and almost nil in the latter. It displaces hydrogen also from boiling solutions of the alkalis, forming aluminates:



In consequence of its very great affinity for oxygen, aluminium displaces from their oxides all the metals below magnesium in the E.-M. series. Thus, when a mixture of aluminium powder and ferric oxide (**thermite**) is placed in a crucible and ignited by means of a piece of burning magnesium ribbon, aluminium oxide and iron are formed:



The very high temperature (about 3000°) produced by the action is sufficient to melt both the iron (m.-p. 1530°) and the oxide of aluminium (m.-p. 2050°). The products, not being miscible, separate into two layers. This very simple method of making pure specimens of metals like chromium, uranium, and manganese, whose oxides are otherwise hard to reduce, is called by Goldschmidt, the inventor, **aluminothermy**. By preheating the ends of steel rails with a gasoline torch, firing a mass of thermite in a crucible above the joint, and allowing the iron to flow into the joint, perfect welds are made. In the same way, large castings, like propeller shafts, when broken, can be mended. The sulphides, such as pyrite, are reduced with equal vigor by aluminium.

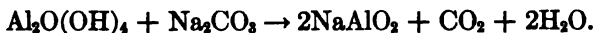
The largest part of the aluminium of commerce is used by steel-makers. When added in small amount (< 1 : 1000) to molten steel, it combines with the gases, and gives sound ingots free from blow holes.

**Aluminium Chloride  $AlCl_3$ .** — If the metal or the hydroxide is treated with hydrochloric acid, and the solution is allowed to evaporate, crystals of  $AlCl_3 \cdot 6H_2O$  are formed. When heated, this hydrate is completely hydrolyzed, hydrochloric acid is given off, and only the oxide remains. The **anhydrous chloride** is much used as a catalytic agent for causing combination in organic chemistry. It is made by passing dry chlorine over aluminium.

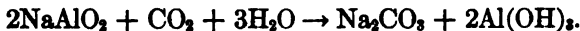
Aluminium chloride gives a vapor pressure of 760 mm. at  $183^\circ$ , and sublimes, as a white crystalline solid, without melting. Under pressure, it melts at  $193^\circ$ . In the mode of preparation described above, it is, therefore, vaporized, and condenses in a cool part of the tube. It fumes when exposed to moist air, on account of the hydrogen chloride produced by hydrolysis, and only with excess of hydrochloric acid does it give a clear solution free from basic salts.

**Aluminium Hydroxide and the Aluminates.** — When an alkali is added to a solution of a salt of aluminium, the **hydroxide**  $Al(OH)_3$  is precipitated in gelatinous form. It loses water gradually when dried, without forming any intermediate hydroxides (p. 634), until  $Al_2O_3$  alone remains. Natural forms of this substance are hydrargyllite  $Al(OH)_3$  ( $= Al_2O_3 \cdot 3H_2O$ ), bauxite  $Al_2O(OH)_4$  ( $= Al_2O_3 \cdot 2H_2O$ ), which always contains ferric oxide, and diasporite  $AlO.OH$  ( $= Al_2O_3 \cdot H_2O$ ).

Commercially, the hydroxide is made by heating bauxite with dry sodium carbonate, or with concentrated sodium hydroxide solution at  $150$ – $170^\circ$ . The ferric oxide, having no tendency to form a carbonate or to interact with a base, remains unchanged. The sodium aluminate which is formed is extracted with water:



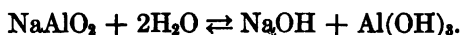
The hydroxide is then precipitated by passing carbon dioxide through the solution:



Aluminium hydroxide, being amphoteric, interacts both with acids and with bases, and is, therefore, like zinc hydroxide (p. 771), ionized both as a base and as an acid. It interacts only slightly with ammonium hydroxide, because this substance is too feebly basic, but, from the solution in the active alkalies, the **aluminates**

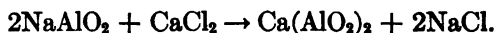


$\text{Na}_3\text{AlO}_3$ ,  $\text{Na}_2\text{AlO}_2$ , and  $\text{KAlO}_2$  can be obtained in solid form. The aluminates are largely hydrolyzed by water:

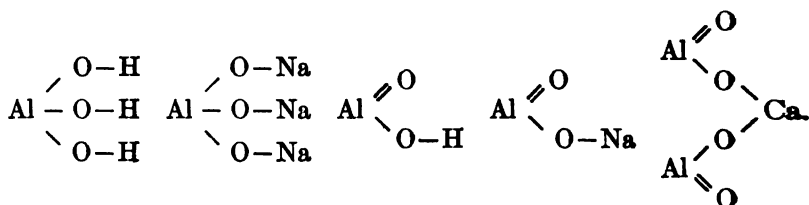


Hence an excess of sodium hydroxide is required for the complete solution of aluminium hydroxide by the reversal of this action. Sodium aluminate is used as a mordant in dyeing (see below), on account of the ease with which the solution gives up aluminium hydroxide when any material is present which can adsorb the free portion of the hydroxide and so cause forward displacement of the above equilibrium.

When calcium chloride is added to a solution of sodium aluminate, the insoluble **calcium metaluminate** is deposited:



The relations of these substances are shown by the following formulæ:



A number of insoluble metaluminates are found in nature. They crystallize in the regular system, and are known as **spinelles**. They contain bivalent metals in place of the calcium in the last-named compound. Thus we have spinelle proper  $\text{Mg}(\text{AlO}_2)_2$ , and **gahnite**  $\text{Zn}(\text{AlO}_2)_2$ . Corresponding and isomorphous derivatives of chromic and ferric hydroxides are chromite  $\text{Fe}(\text{CrO}_2)_2$  and magnetite  $\text{Fe}(\text{FeO}_2)_2$ .

**Aluminium Oxide  $\text{Al}_2\text{O}_3$ .** — The oxide (**alumina**) is made by heating the pure hydroxide made from bauxite (see above). It is found in nature in pure form as corundum. This mineral is only one degree less hard than the diamond. Emery is a common variety, contaminated with ferric oxide, and was widely used as an **abrasive** until largely displaced by carborundum. The ruby is pure aluminium oxide tinted by a trace of a compound of chromium, while the **sapphire** is the same material colored with aluminates of iron and titanium. It is said, however, that the same tint is conferred upon

colorless corundum by exposure to the influence of salts of radium. By allowing the pulverized oxides to be carried by the stream of oxygen of an oxy-hydrogen blowpipe, and placing a disc in the flame to catch the molten particles, "synthetic" sapphires and rubies are now made in large quantities. **Alundum**, a refractory material for crucibles, is made by heating objects made of the oxide in the electric furnace until a small proportion of the material is melted. The alumina made by gently heating the hydroxide interacts easily with acids, but after being strongly heated it resembles natural alumina in being very slowly affected by them. Minerals containing insoluble compounds of aluminium are attacked when heated strongly with potassium bisulphate (*cf.* p. 674), the sulphate of aluminium being formed.

**Aluminium Sulphate: The Alums.** — Aluminium sulphate  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  is prepared by treating either bauxite or pure clay (kaolin) with sulphuric acid. In the latter case the insoluble residue of silicic acid is removed by filtration:



The solution of the sulphate is acid in reaction. It crystallizes in leaflets which, when the source was clay or bauxite, have a yellow tinge due to the presence of iron as an impurity. The salt is used as a source of precipitated aluminium hydroxide in paper-making, water purification, and dyeing.

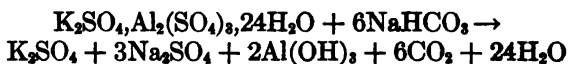
When potassium sulphate solution is added to a strong solution of aluminium sulphate, octahedral crystals of potash alum,  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  are deposited. This is a double salt, and is one of a large number known as the **alums**. These have the general formula  $\text{M}_2'\text{SO}_4 \cdot \text{M}_2''(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , and may be made as above by using a sulphate of a univalent metal with one of a trivalent metal. Thus, for  $\text{M}'$  we may use K,  $\text{NH}_4$ , Rb, Cs, and  $\text{Ti}^I$ , and for  $\text{M}''$ , Al,  $\text{Fe}^{III}$ ,  $\text{Cr}^{III}$ ,  $\text{Mn}^{III}$ , and  $\text{Ti}^{III}$ . We may even employ selenates, such as  $\text{K}_2\text{SeO}_4$ . All of the resulting double salts are isomorphous, and a crystal of one will continue to grow in a solution of another, acquiring, of course, an outer layer of different composition, but of the same crystallographic orientation.

**Potassium-Aluminium Sulphate  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ .** — Ordinary alum is made from aluminium sulphate obtained from clay (see above). It is also prepared by heating alunite, a basic

alum found near Rome and in Hungary, and extracting the product with hot water. The alunite, having the composition  $\text{KAl}_2(\text{OH})_6(\text{SO}_4)_2$ , leaves an insoluble residue of the hydroxide, mixed with ferric oxide which is present as an impurity:



The saturated solution of alum contains, at  $10^\circ$ , 9 parts of the anhydrous salt in 100 parts of water, and at  $100^\circ$ , 422 parts in 100 of water. The hydrated salt melts at  $90^\circ$ . An aqueous solution of this salt or of sodium phosphate (p. 559) is used for fire-proofing draperies, because the crystals deposited in the fabric melt easily, and the fused material protects the fibers from access of oxygen. When heated more strongly alum loses its water of hydration, together with some sulphur trioxide, and leaves a slightly basic, anhydrous salt known as **burnt alum**. A solution of alum dissolves a considerable amount of aluminium hydroxide, giving "neutral alum," a basic salt  $\text{K}_2\text{SO}_4, \text{Al}_2(\text{OH})_6(\text{SO}_4)_3$  used as a mordant (see p. 820). The substance is usually prepared by adding sodium carbonate to the solution of alum as long as the aluminium hydroxide, formed locally, continues to redissolve. Potash-alum and ammonium-alum are more easily freed from impurities (*e.g.*, compounds of iron) by recrystallization than is aluminium sulphate, and the alums are therefore used instead of the latter in medicine, in dyeing delicate shades, and to replace cream of tartar in baking powder (p. 689). In the last case, the reaction



liberates carbon dioxide by hydrolysis of the aluminium carbonate.

**Hydrolysis of Aluminium Carbonate.**—The foregoing action, and others discussed above (p. 808), show that the carbonate is *completely* hydrolyzed:

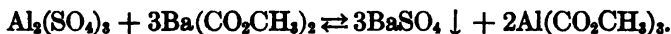


It will be seen that this may be due only *in part* to the feebly basic qualities of the hydroxide. If the hydroxide were not precipitated, it would cause some reversal of the action, and *some* of the carbonate would remain. The insolubility of one product explains also other cases of the complete hydrolysis of salts (*e.g.*, ammonium silicate, p. 648, and next section).

**Aluminium Sulphide  $Al_2S_3$ .** — This compound is most easily obtained by mixing pyrite with aluminium powder and igniting with magnesium ribbon (p. 653):  $3FeS_2 + 4Al \rightarrow 2Al_2S_3 + 3Fe$ . It forms a grayish-black solid, and is hydrolyzed by water as is magnesium sulphide, giving the hydroxide and hydrogen sulphide. On this account, the sulphide, like magnesium sulphide (p. 767), cannot be formed by precipitation in presence of water. Thus, ammonium sulphide with a salt of aluminium, in solution, gives a precipitate of aluminium hydroxide:



**Aluminium Acetate.** — This salt is used by dyers, because, being a salt of a weak base and a weak acid, it is much hydrolyzed by water, especially at  $100^\circ$ . In mordanting, it thus gives aluminium hydroxide very easily. It is made by treating lead or barium acetate with aluminium sulphate, and filtering and crystallizing the solution:



**Coagulation Method of Purifying Water: Sizing Paper.** — When aluminium hydroxide is formed, it gives first a colloidal suspension, which coagulates to a gelatinous precipitate. When this precipitate is produced in water used for domestic purposes, and containing fine, suspended matter, the gelatinous material causes the fine particles to collect into larger ones which settle rapidly, and permits the use of relatively small settling ponds. These larger particles enclose also practically all the bacteria. If the water is slightly hard, crude aluminium sulphate, alone, is used:



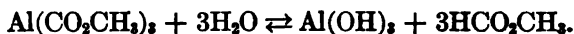
If the water is very soft, a little lime  $Ca(OH)_2$  is added. The few remaining organisms (particularly colon bacilli, p. 142) are destroyed by later addition of bleaching powder or of chlorine-water (p. 226).

In some localities crude ferrous sulphate, obtained as a by-product in cleaning iron, is cheaper, and is employed instead. The lime precipitates ferrous hydroxide  $Fe(OH)_2$ . This is quickly oxidized to colloidal ferric hydroxide  $Fe(OH)_3$ , which coagulates the suspended matter.

Aluminium hydroxide is employed also in **sizing** cheaper grades of **paper** (p. 603), an operation required to prevent the absorption

and consequent spreading of the ink. For writing-paper, gelatine solution is employed. In making printing-papers, rosin soap (made by dissolving rosin in caustic soda) is mixed with the paper-pulp, and aluminium sulphate is added. The rosin and aluminium hydroxide are precipitated in the pulp, and pressing between hot rollers afterwards melts the former and gives a surface to the paper.

Delicate cloth goods are rendered waterproof by saturating them with aluminium acetate solution and then steaming them to promote hydrolysis. The aluminium hydroxide is thus precipitated in the capillaries of the cotton or linen and renders them non-absorbent:



**Kaolin and Clay: Earthenware and Porcelain.**—By the action of water and carbon dioxide upon granite, and other rocks containing feldspar  $\text{KAlSi}_3\text{O}_8$ , the potash is slowly removed, and the compound is changed largely into a hydrated orthosilicate  $\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$ . When pure, it forms **kaolin** or china clay, a white, crumbly material. When washed away and redeposited, it usually acquires compounds of iron, the carbonates of calcium and magnesium, and sand (silica), becoming common clay. Ocher, umber, and sienna are clays colored with oxides of iron and manganese. Fuller's earth is a purer variety.

The plasticity of clay, a property connected with the colloidal nature of the kaolin, enables it to be fashioned into various shapes. When heated, it shrinks and becomes a hard, solid, porous mass, and does not melt. These two properties enable us to use it in making bricks, pottery, and porcelain. The presence of calcium and magnesium compounds makes the clay more fusible, because it permits the formation of fusible silicates of these metals. **Bricks** and **tiling** for roofs and drains are made of common clay and, when red, owe their color to oxide of iron  $\text{Fe}_2\text{O}_3$ . The firing is done with fuel gas in ovens or kilns of brickwork. The efflorescence which often appears on the surface of the bricks ("niter") is generally due to sodium sulphate or sodium chloride present originally in the clay. To glaze drain pipes and some bricks, salt is thrown into the kiln. The water vapor, at a red heat, hydrolyzes the vapor of the salt, hydrogen chloride is set free, and the sodium hydroxide gives with the clay a fusible sodium-aluminium silicate which fills the surface pores. Clay for fire brick (infusible) must contain silica, but no lime.

**China** and **porcelain** are made from pure clay, free from iron, to which a little of the more fusible felspar is added. After the first firing, the articles are porous (bisque), and must be covered with a glaze to make them water-tight. A paste of finely ground felspar and silica, sometimes containing lead oxide, is spread on the surface, and the articles are fired again, at a higher temperature. The felspar melts and fills the pores, so that a continuous, semi-transparent material results. Colored decorations are added by means of suitable materials, mainly oxides of metals which give colored silicates. The third firing causes these oxides to interact and fuse with the glaze. Porcelain, if made with sufficient clay, is very infusible. It is attacked by aqueous and by fused alkalis, however, giving soluble silicates.

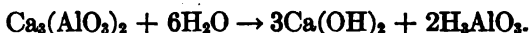
The Schwerin process for separating ferric oxide  $\text{Fe}_2\text{O}_3$  from clay, so that white porcelain may be obtained, is now used on a large scale and affords an interesting application of the properties of colloidal suspensions (p. 622). When the impure clay is suspended in water, the particles of ferric oxide are positively charged and those of the clay are negative. By inserting plates connected with the dynamo in the trough, the clay particles are caused to drift towards the positive plate and the ferric oxide towards the other, so that, when the liquid from the positive end is allowed to settle, pure clay is obtained.

In making bricks, in some cases, advantage is taken of the fact that negative colloids, such as clay, become more strongly negative in presence of a trace of free alkali. Thus, when a trace of sodium hydroxide is added to clay slip, the particles repel one another more strongly, the cohesion which causes the plasticity is reduced, and the clay can be poured into molds. This avoids diluting the clay with water, which would only have to be driven out again, with great waste of heat, in the firing.

**Cement.** — Cement is made by heating limestone  $\text{CaCO}_3$ , clay  $\text{HAlSiO}_4$ , and sand  $\text{SiO}_2$ , or a natural rock containing all three in the right proportions. Such a rock, made into cement by volcanic heat, was quarried by the Romans near Naples and elsewhere, and its capacity for hardening even under water was utilized by them. Blast-furnace slag, when pulverized and heated with limestone, has been found to yield an excellent quality of cement, and a valuable use has thus been found for what was formerly an annoying encumbrance. The mixture, or the pulverized natural rock, is moistened

and fed slowly in at the upper end of an inclined ( $6^\circ$ ) revolving cylinder of iron (20 to 45 by 2 meters). The motion continually turns over the thin layer, and exposes every particle to the heat of the air-blast, charged with pulverized coal, burning in the interior. The product slides out in a continuous stream at the lower end, and is pulverized by steel balls in a ball mill.

Cement is held to be a mixture of calcium silicate and calcium aluminate. The former is simply a filler. The latter is hydrolyzed by the water:



The calcium hydroxide slowly crystallizes, connecting the particles of the calcium silicate. The aluminium hydroxide fills the interstices and renders the whole compact and impervious.

**Ultramarine.** — Formerly, pulverized *lapis lazuli*, a rare mineral of beautiful blue color, was used by artists as a pigment. Gmelin (1828) found a way of making it artificially. A mixture of kaolin, sodium carbonate, sulphur, and charcoal is heated until a green mass is obtained. The mass is then pulverized and heated with more sulphur. Its composition is approximately  $4\text{NaAlSiO}_4, \text{Na}_2\text{S}_2$ . The product is used as laundry blueing, in making blue-tinted paper, and with oil in making paint. It is also added in small amount to correct the natural yellow tint of linen, starch, sugar (p. 606), and paper-stock. By varying the mode of heating, without altering the composition, various colors from green to reddish violet can be obtained. No pure colored substance can be extracted from it. The variety of colors is due to different degrees of colloidal dispersion of some substance suspended in the solid, just as gold, which is pale yellow in mass, gives colloidal suspension (p. 621) of different colors (red, purple, or blue) according to the fineness of the particles (*cf.* p. 750).

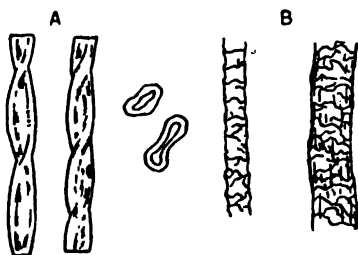


FIG. 158.

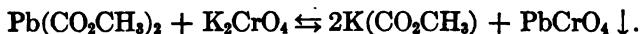
**Dyeing.** — The problem of the dyer is to confer the desired color upon a fabric made, usually, of cotton, linen, wool, or silk, and to do

this in such a way that the dye is fast to (*i.e.*, is not removed or destroyed by) rubbing and light, and often, also, to washing with

soap. To understand the means by which this is achieved, it must be noted that cotton and linen consist of smooth hollow fibers (Fig. 158A) of the composition of cellulose ( $C_6H_{10}O_5$ )<sub>n</sub>. Wool is made of hollow fibers, with a scaly surface (B) and silk ( $C_{15}H_{22}N_5O_8$ )<sub>n</sub> of solid filaments, but both are composed of proteins (p. 628). Now, the proteins are much more active chemically than is cellulose, and also, as colloidal materials, seem to have a much greater tendency to adsorb other substances than has cellulose. Hence, accidental stains on wool or silk are much less often removable than are those on cotton, and when samples of the three materials are dipped in a solution of a dye, the first two are permanently dyed, while from the last most dyes can be completely washed out with water.

Three modes of dyeing may be mentioned:

1. **Insoluble Dyes.** If the colored body can be produced by *precipitation*, after the solution has filled the capillary and wall of every fiber of the goods, then, if the dye is sufficiently insoluble, it is mechanically imprisoned in every fiber and cannot be washed out. This plan may be applied to any kind of goods. For example, if cotton, silk, or wool is first boiled in a solution of lead acetate, and is then soaked in a boiling solution of potassium chromate, it is dyed a brilliant, permanent yellow. Lead chromate is the colored body:



The part precipitated on the outside of the goods can be, and is, at once washed off by rubbing in water, but the particles inside the fibers can come out only by being dissolved, and they are insoluble in water. **Indigo**  $C_{16}H_{10}N_2O_2$ , which is used in larger amounts than any other dye, belongs to this class. Obtained in early times from several points in Europe and Egypt, where it was known as woad, and more recently imported from India, where the cultivation of the indigo plant was as important an industry as is the growing of cotton in the Southern States, it is now almost all made artificially. Synthetic indigo has been manufactured since 1907, with naphthalene  $C_{10}H_8$  (p. 613), obtained from gas tar and the tar from by-product coke ovens, as the initial substance. The cloth is saturated with an alkaline solution of indigo white  $C_{16}H_{12}N_2O_2$  (cf. p. 444), a soluble, slightly acid substance, and the oxygen of the air subsequently oxidizes this and deposits the insoluble indigo blue within the fibers:





Indanthrene blue is applied in the same way as indigo, and is even less affected by light.

**2. Mordant or Adjective Dyes.** Since cotton is inactive chemically and, although a colloid, has but a slight tendency to adsorb dyes, it is usually necessary first to introduce into the fibers of cotton some colloidal substance with greater adsorptive powers. Substances of this kind are tannic acid for basic dyes, and gelatinous colloidal hydroxides, such as those of aluminium, tin, iron, and chromium, for non-basic (including acid) dyes. They are called **mordants** (Lat. *mordere*, to bite). Thus, if in three jars we place very dilute solutions of aluminium sulphate, ferric chloride  $\text{FeCl}_3$  and chromous acetate  $\text{Cr}(\text{CO}_2\text{CH}_3)_2$ , then add a few drops of a solution of a dye to each, and finally introduce a little of a base (like sodium hydroxide) to precipitate the hydroxide of the metal, this hydroxide will adsorb the dye and carry it into the precipitate. Such a precipitate of mordant and dye is called a **lake** (Fr. *laque*, lac). With the same dye, the three lakes have *different colors*. Thus, in the above mentioned experiment, if **alisarin**  $\text{C}_{14}\text{H}_5\text{O}_4$  (madder), an orange-yellow, slightly soluble acid, is used as the dye, the colors are red (Turkey red), violet, and maroon, respectively. This, of course, is due to the different degrees of dispersion in the three colloidal materials. If aluminium hydroxide is to be used, by first saturating the cloth with hot aluminium acetate solution (p. 815), or by using first aluminium sulphate and then ammonium hydroxide, the aluminium hydroxide is precipitated within the fibers of the goods. When the material is then dyed, the coloring matter is adsorbed by the mordant, with which it forms an insoluble lake, within the fibers. **Cochineal**, obtained from wingless, female insects found on the variety of cactus bearing this name, contains carminic acid  $\text{C}_{11}\text{H}_{12}\text{O}_7$ , and gives a red lake with aluminium hydroxide. Basic dyes, like Malachite green and Methylene blue, behave similarly with tannic acid, or an insoluble salt of tannic acid, as mordant. It will be seen that, so far as the fabric is concerned, this process, like the first, is a mechanical one, and is independent of the chemical nature of the goods.

**3. Direct or Substantive Dyes.** Most organic dyes are direct dyes on silk or wool, and require no mordant with these materials. The actions seem to be sometimes chemical, but more often cases of adsorption by the silk or wool (both colloids) themselves. A few dyes are also fast on cotton. **Congo-red**  $\text{Na}_2\text{C}_{20}\text{H}_{12}\text{N}_6\text{S}_2\text{O}_6$  is fast both on cotton and wool, but is no longer much used. Chry-

sophenin is now one of the commonest dyes of this class. These dyes, which are sodium salts of complex organic acids, are colloids like soap (p. 623) and are salted out *within* the fibers of the goods by adding sodium sulphate to coagulate them and assist the adsorption by the cotton. Once adsorbed in this way, unlike soap, they cannot be washed out.

**Analytical Reactions of Aluminium Compounds.** — The alkalies, and alkaline solutions like that of ammonium sulphide, precipitate the white hydroxide (p. 815). The product is soluble in excess of the active alkalies. Soluble carbonates also throw down the hydroxide. Aluminium compounds, when heated strongly in the flame with cobalt salts, give a blue aluminate of cobalt  $\text{Co}(\text{AlO}_2)_2$ , Thenard's blue.

**Exercises.** — 1. What are the differences between zinc and aluminium, and their corresponding compounds?

2. Construct equations showing, (a) the hydrolysis of aluminium sulphate (p. 813), (b) the interaction of aluminium sulphate and cobalt nitrate in the Bunsen flame.

3. Formulate the ionization of aluminium hydroxide (pp. 771, 811).

4. Why does zinc hydroxide, in spite of its feebleness as a base, dissolve in ammonium hydroxide, while aluminium hydroxide does not?

## CHAPTER XL

### GERMANIUM, TIN, LEAD

THE elements on the right side of the fifth column of the periodic table, aside from carbon and silicon, are **germanium** (Ge, at. wt. 72.5), **tin** (Sn, at. wt. 118.7), and **lead** (Pb, at. wt. 207.2). **Titanium** (Ti, at. wt. 48.1), **zirconium** (Zr, at. wt. 90.6), **cerium** (Ce, at. wt. 140.25), and **thorium** (Th, at. wt. 232.4) occupy the left side.

*The Chemical Relations of the Family.*— All of these elements show a maximum valence of four. Germanium, tin, and lead are also bivalent. In this respect they resemble carbon and differ from silicon, which is more closely allied to the elements on the left side of the column. The oxides and hydroxides in which these three elements are bivalent become more basic, and the elements themselves more metallic in chemical relations, with increase in atomic weight. In this they resemble the potassium and calcium families. Curiously enough, the same three hydroxides are also acidic. They are more strongly acidic than is zinc hydroxide, for the salts they form by interaction with bases are less hydrolyzed than are the zincates. This acidic character likewise increases in the order in which the elements are named above.

### GERMANIUM GE

**Germanium** (cf. p. 465) may be described as a transition element between carbon and tin. It forms two oxides  $\text{GeO}$  and  $\text{GeO}_2$  corresponding to those of carbon and of tin. **Germanious oxide** is not very definitely basic or acidic, and the sulphide is the only other well-defined compound of this set. **Germanic oxide** and hydroxide are acidic entirely. The resemblance to carbon is shown in the formation of an unstable compound with hydrogen, and of **germanium chloroform**  $\text{GeHCl}_3$ . Like carbon, tin, and silicon, germanium gives a volatile **chloride**  $\text{GeCl}_4$  (b.-p.  $87^\circ$ ). Like tin and gold (p. 760), it forms **complex sulphides** derived from germanic sulphide, such as  $\text{K}_2\text{GeS}_3$ . The element was discovered (in 1886) in argyrodite, a complex sulphide  $4\text{Ag}_2\text{S} \cdot \text{GeS}_2$ .

## TIN SN

**The Chemical Relations of the Element.** — Tin is both bivalent and quadrivalent. Each of the hydroxides,  $\text{Sn}(\text{OH})_2$  and  $\text{SnO}(\text{OH})_2$  (or  $\text{Sn}(\text{OH})_4$ ), is both basic and acidic, so that there are really four series of compounds. Still, stannous hydroxide is mainly a base, of a feeble sort, while stannic hydroxide is mainly an acid. Thus we have stannous chloride, sulphate, and nitrate, which are stable, although they are all more or less hydrolyzed by water, and sodium stannite  $\text{Na}_2\text{SnO}_2$  which is unstable. On the other hand, stannic nitrate, sulphate, and chloride are completely hydrolyzed by water, while sodium stannate  $\text{Na}_2\text{SnO}_3$  is comparatively stable. The dioxide  $\text{SnO}_2$  is an infusible solid, and resembles, therefore, silicon dioxide. Tin has a tendency to give complex acids and salts, like  $\text{H}_2\text{SnCl}_6$ ,  $(\text{NH}_4)_2\text{SnCl}_6$ ,  $\text{H}_2\text{SnI}_6$ ,  $\text{K}_2\text{SnF}_6$ , but these are ionized also to a small extent after the manner of double salts, giving ions of  $\text{Sn}^{++++}$ . Tin forms no compounds with hydrogen and no salts with weak acids, like carbonic acid.

**Occurrence and Extraction.** — Tin has long been in use, specimens of it being found in Egyptian tombs. The chief ore of tin is tin-stone, or cassiterite  $\text{SnO}_2$ , which consists of square prismatic crystals whose dark color is due to the presence of iron compounds. The ore is roughly pulverized and washed, to remove granite or slate with which it is mixed, and is then roasted, to oxidize the sulphides of iron and copper, and drive off the arsenic which it contains. After renewed washing to eliminate sulphate of copper and oxide of iron, it is reduced with coal in a reverberatory furnace. The tin is afterwards remelted at a gentle heat, and the pure metal flows away from compounds of iron and arsenic. The production (1914) was: Straits Settlements 70,000 short tons, Bolivia 21,000, Banka 10,400, Cornwall 6720, Nigeria (alluvial) 5600.

**Physical and Chemical Properties.** — Tin is a silver-white, crystalline metal of low tenacity but great malleability (tin-foil). Its density is 7.3, and its melting-point about  $232^\circ$ . Tin is dimorphous (p. 412). In 1851, the tin pipes of an organ were found to have turned largely into a gray powder. In 1868 a shipment of blocks of tin stored in the custom house in Petrograd was found to have changed in the same way. Objects of tin in museums frequently show spots indicating the presence of the "tin pest," as it was called. It now appears that white, metallic tin is stable only above  $18^\circ$ , and

that below this temperature it is unstable and is liable to change into gray tin of lower density (5.85). This transition point is similar to that of sulphur at 96° (p. 412). By immersing the tin in a solution of pink-salt (see below), the change is hastened. When the two kinds of tin are used as the poles of a cell, and are surrounded by pink-salt solution, no difference in potential is observed at 18°. But below 18°, white tin, being unstable, is more active and becomes negative (giving positive ions), while above 18°, gray tin becomes negative.

Tin-plate (*cf.* p. 800) is made by dipping carefully cleaned sheets of mild steel into molten tin. Vessels of copper are also coated, internally, with tin, to prevent the formation of the basic carbonate (p. 738). For this purpose they are cleaned with ammonium chloride, sprinkled with rosin (to reduce the oxide), and heated to 230°. Molten tin is then spread on the surface with a piece of tow. Common pins are made of brass wire, and are coated with tin by being shaken in a solution containing a salt of this metal. The zinc in the alloy displaces some of the tin, and this is deposited on the surface of the brass. Alloys of tin, such as bronze (p. 738), soft solder (50 per cent lead), pewter (25 per cent lead), and britannia metal (10 per cent antimony and some copper), are much used in the arts. On account of the action of soft water containing dissolved oxygen on lead (see p. 830), tin pipes are preferred for distributing distilled water and for beer pipes.

Much tin is now recovered by treating old "tin cans" and scrap tin-plate with dry chlorine. The dried gas converts the tin into stannic chloride  $\text{SnCl}_4$ , which is used to make mordants, but hardly attacks the iron (p. 222). The process is called **detinning**.

Tin, although it displaces hydrogen from dilute acids, is not tarnished by moist air. With warm hydrochloric acid it gives stannous chloride  $\text{SnCl}_2$  and hydrogen. Hot, concentrated sulphuric acid forms stannous sulphate  $\text{SnSO}_4$  and sulphur dioxide. Nitric acid, when cold and very dilute, interacts with it, giving stannous nitrate, and a portion of the nitric acid is reduced to ammonia (*cf.* p. 534):



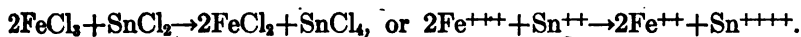
With concentrated nitric acid, stannic nitrate is formed, but most of this salt is hydrolyzed by the water at the high temperature of the action (*cf.* p. 648), and metastannic acid  $(\text{H}_2\text{SnO}_3)_x$  ( $\beta$ -stannic acid) remains. The final result is therefore shown by the equation (simplified):



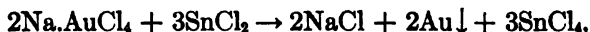
The white, insoluble product continues to give nitric acid during prolonged washing, and seems therefore to contain some basic nitrate. Tin also displaces hydrogen from caustic alkalies, giving metastannates, such as sodium metastannate  $\text{Na}_2\text{SnO}_3$ .

**Stannous Chloride  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ .** — This salt is made by the interaction of tin and hydrochloric acid. When the colorless crystals are heated, or when a strong aqueous solution is diluted, the salt is partially hydrolyzed. In the latter case the basic chloride  $\text{Sn}(\text{OH})\text{Cl}$  is deposited. By presence of excess of hydrochloric acid, the hydrolysis is prevented. The solution is used as a mordant (p. 820).

Stannous chloride tends to pass into stannic chloride  $\text{SnCl}_4$ , and is therefore an active reducing agent. Thus, it reduces the chlorides of mercury (p. 778) and of the noble metals, liberating the free metals. The action is of the form  $\text{Hg}^{++} + \text{Sn}^{++} \rightarrow \text{Hg} + \text{Sn}^{++++}$ . Stannous chloride reduces cupric and ferric chlorides to the cuprous and ferrous conditions in like manner:

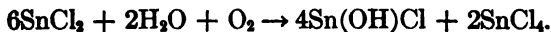


When stannous chloride solution is added to a solution of sodium chloraurate  $\text{Na}.\text{AuCl}_4$ , the former reduces the latter, and metallic gold is liberated. The stannic chloride which is formed:



is hydrolyzed by the water (see below), and the colloidal stannic acid is precipitated, with colloidal gold finely dispersed upon it. The strongly colored precipitate is called **purple of Cassius**, and is obtained with different tints, often red, according to the degree of dispersion. It is used for gilding porcelain.

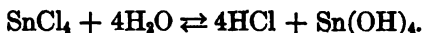
Stannous chloride also reduces free oxygen, or, what is the same thing, is oxidized by the air. In this case, stannic chloride is formed in an acidified solution and the liquid remains clear; in the neutral solution a precipitate of the basic chloride is formed as well:



Powdered tin, if placed in the bottle along with the acid solution, will undo the effects of this action by reducing the stannic salt to the stannous condition once more.

**Stannic Chloride  $\text{SnCl}_4$ .** — When chlorine acts upon tin, or upon stannous chloride (either solid or dissolved), stannic chloride is

formed. The compound is a colorless liquid (b.-p.  $114^{\circ}$ ) which fumes very strongly in moist air, giving hydrochloric acid and stannic acid. It was formerly known, after its discoverer (1605), as *spiritus fumans Libavii*. The aqueous solution, when freshly made, has almost no conductivity, and the compound is therefore very slightly ionized. As hydrolysis proceeds, the conductivity increases, but the hydrochloric acid is the conducting substance. After a time hydrolysis becomes almost complete. The stannic acid which is formed is not precipitated, however, but remains in colloidal suspension:



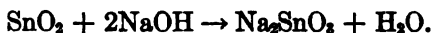
The chloride, with small amounts of water, gives crystalline hydrates  $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , and  $\text{SnCl}_4 \cdot 8\text{H}_2\text{O}$ , of which the second is used as a mordant under the name "oxymuriate" of tin. The double (or perhaps complex) salts such as ammonium-stannic chloride or "pink-salt"  $(\text{NH}_4)_2\text{SnCl}_6$  are easily made. Pink salt is used as a mordant on cotton, and gives a red lake with alizarine (p. 820).

**Stannic bromide**  $\text{SnBr}_4$  (m.-p.  $30^{\circ}$ , b.-p.  $201^{\circ}$ ) is soluble in water.

**$\alpha$ -Stannic Acid and its Salts.** — When a solution of stannic chloride is treated with ammonium hydroxide, a white, gelatinous precipitate is formed. To this the formula  $\text{H}_2\text{SnO}_3$  is generally assigned:



It is, however, in reality, amorphous, and loses water gradually until the dioxide remains. Thus, neither  $\text{Sn}(\text{OH})_4$  nor  $\text{SnO}(\text{OH})_2$  is obtainable as a definite compound (p. 635). When stannic oxide is fused with caustic soda, a *metastannate*, namely, the  $\alpha$ -stannate  $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ , is formed:



This compound is used as a mordant under the name of "preparing salt." When its solution is acidified,  $\alpha$ -stannic acid, the actual mordant, is formed by double decomposition. This  $\alpha$ -stannic acid interacts readily with acids and alkalies, and the chloride obtained from it is identical with stannic chloride described above.

Flannelette and other cotton goods are rendered non-inflammable by saturation first with sodium  $\alpha$ -stannate solution and then, after drying, with ammonium sulphate. The acid is too feeble and too insoluble to form an ammonium salt:



The sodium sulphate is washed out and the goods, after being dried, contain stannic oxide. The latter cannot afterwards be removed by washing, and the material is permanently fireproof. Silk is also loaded with stannic oxide, the amount used varying from 25 (better shades on dyeing) to 300 per cent or more.

The  $\alpha$ -stannates of the metals, aside from those of potassium and sodium, like the silicates and carbonates which they much resemble, are all insoluble in water, and may be made by double decomposition.

**$\beta$ -Stannic Acid, or Metastannic Acid.** — The product of the action of nitric acid upon tin is a hydrated stannic oxide like the foregoing substance, but is not identical with it. It does not easily interact with alkalis. By boiling it with caustic soda, however, and then extracting with pure water, a soluble sodium  $\beta$ -stannate,  $\text{Na}_2\text{Sn}_3\text{O}_{11}$ , is obtained.  $\beta$ -stannic acid is also very slowly attacked by acids, and the chloride secured from it is not identical with the ordinary chloride. For these reasons it is supposed to be a hydrate of a polymer of stannic oxide  $(\text{SnO}_2)_x \cdot x\text{H}_2\text{O}$ . When fused with caustic soda, it gives the same  $\alpha$ -stannate as does the dioxide itself.

The difference between the properties of the two stannic acids was noticed by Berzelius (1811), and was the first case in which identity in composition was found not to be accompanied by identity in properties (*cf.* Isomers, p. 583).

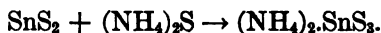
**The Oxides of Tin.** — When stannous oxalate is heated in absence of air, stannous oxide remains:  $\text{SnC}_2\text{O}_4 \rightarrow \text{SnO} + \text{CO}_2 + \text{CO}$ . It is a black powder which burns in the air, giving the dioxide. The corresponding hydroxide  $\text{Sn}_2\text{O}(\text{OH})_2$  is formed by adding sodium carbonate to stannous chloride solution. It is a white powder, easily dehydrated, and interacts with alkalis to give soluble stannites, such as  $\text{Na}_2\text{SnO}_3$ . When the solution is boiled, tin is deposited, and sodium stannate is formed, the behavior resembling that of cuprous oxide when heated with oxygen acids (p. 743). With acids, the hydroxide gives stannous salts.

**Stannic oxide**  $\text{SnO}_2$  is found in nature (p. 823), and may be made in pure form by igniting  $\beta$ -stannic acid. When heated, it becomes yellow, but recovers its whiteness when cooled (*cf.* Zinc oxide, p. 770). Prepared at a low temperature, it interacts easily with acids, but after strong ignition, is affected by them very slowly.

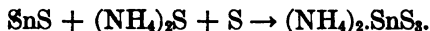


**The Sulphides of Tin.** — **Stannous sulphide**  $\text{SnS}$  is obtained as a dark-brown precipitate when hydrogen sulphide is led into a solution of a stannous salt.

**Stannic sulphide**  $\text{SnS}_2$  is formed likewise by precipitation, and is yellow in color. It is made also by heating together tin filings, mercury, sulphur, and ammonium chloride. The mercury and ammonium chloride are ultimately volatilized, and the stannic sulphide remains in the form of yellow, crystalline scales ("mosaic gold" or "bronze powder"). Stannic sulphide loses sulphur when strongly heated, and leaves stannous sulphide. It is not much affected by dilute acids, but interacts with solutions of ammonium sulphide (or sodium sulphide), giving soluble **complex sulphides**, such as **ammonium sulphostannate**:



The corresponding **sodium sulphostannate** is easily crystallized in the form  $\text{Na}_2\text{SnS}_3 \cdot 2\text{H}_2\text{O}$ . Stannous sulphide is not affected by soluble sulphides, but polysulphides, such as yellow ammonium sulphide, give with it the above mentioned sulphostannates:



With acids the sulphostannates undergo double decomposition, but the free acid  $\text{H}_2\text{SnS}_3$  thus produced is unstable and breaks up, giving off hydrogen sulphide, and depositing stannic sulphide.\*

**Analytical Reactions of Salts of Tin.** — The two ionic forms of tin,  $\text{Sn}^{++}$  and  $\text{Sn}^{++++}$ , are both colorless. Their behavior is different. They give a brown and a yellow sulphide, respectively, with hydrogen sulphide. The interaction of these sulphides with yellow ammonium sulphide distinguishes them (*cf.* p. 828) from those of cadmium, copper, and other metals whose sulphides are similarly inactive towards dilute acids. The sulphides of arsenic, antimony, and gold (*q.v.*), however, behave like those of tin in this respect. The reducing power of stannous-ion  $\text{Sn}^{++}$  is very characteristic (p. 825). Zinc displaces tin from solutions of its salts. The oxides are reduced by charcoal in the reducing part of the Bunsen flame and the metal is liberated.

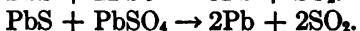
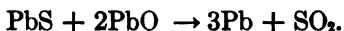
\* These and similar compounds are often called thiostannates, orthothionimmonates, etc. The prefix sulpho- gives more euphonious words, however, and is used here for all excepting the thiocyanates.

## LEAD Pb

**The Chemical Relations of the Element.** — Lead is both bivalent and quadrivalent. The oxides  $\text{PbO}$  and  $\text{PbO}_2$ , and the corresponding hydrated oxides, are both basic and acidic. Lead monoxide is a fairly active base, comparable with cupric oxide, and lead dioxide a feeble one. Both are feebly acidic. The salts of bivalent lead, like  $\text{Pb}(\text{NO}_3)_2$ , commonly called the plumbic salts, are somewhat hydrolyzed by water, but less so than are those of tin. The tetrachloride and other salts of quadrivalent lead are completely hydrolyzed. The plumbites  $\text{Na}_2\text{PbO}_2$  and plumbates  $\text{Na}_2\text{PbO}_3$  are hydrolyzed to a considerable extent. All the compounds in which lead is quadrivalent give up half of the negative radical readily, and are reduced to the "plumbic" condition. The metal displaces hydrogen with difficulty, and is easily displaced by zinc. Lead compounds are all poisonous, and the effects of repeated, very minute doses are cumulative — resulting in "lead colic." For this reason, the manufacture of white lead is forbidden by law in France, and is subject to strict regulation in other countries.

**Occurrence and Metallurgy.** — Commercial lead is almost all obtained from galena  $\text{PbS}$ , which crystallizes in cubes. This ore often contains considerable amounts of silver sulphide  $\text{Ag}_2\text{S}$  (cf. p. 749), which is isomorphous with it, and it occurs in association with sulphides of arsenic, antimony, zinc, copper, and iron. Other salts of lead are of less common occurrence.

The sulphide of lead is first roasted until a sufficient proportion of it has been converted into the oxide and sulphate. The furnace-doors are then closed, and the temperature raised in order that these products may interact with the unchanged part of the sulphide:



Another plan consists in heating galenite with scrap iron or iron ores and coal:  $\text{PbS} + \text{Fe} \rightarrow \text{Pb} + \text{FeS}$ . The molten ferrous sulphide rises to the top as a matte.

The purification of the lead from the other metals whose sulphides have been reduced at the same time is often troublesome. In Parke's process (p. 749) for the extraction of the silver by means of zinc, the greater part of the foreign metals, with the exception of bismuth, passes into the zinc scum. About 0.5 per cent of zinc remains in the lead, and is oxidized by the action of a jet of steam before the lead is



poured into the molds. Lead is refined electrolytically by the Betts process. Heavy plates of the crude lead form the anodes, thin sheets of pure lead the cathodes, and a solution of lead fluosilicate  $\text{PbSiF}_6$ , the cell liquid. The operation is similar to that for refining copper (p. 747). Silver, gold, and bismuth are left as a sludge, while Zn, Co, Ni, and Fe go into solution and are not redeposited.

The production (1913) was: United States 412,000 short tons, Spain 224,000, Germany 199,000, Australia 128,000.

**Physical and Chemical Properties.** — Metallic lead is gray in color, very soft, and of small tensile strength. Its density is 11.4, and its melting-point  $327.4^\circ$ . While warm, it is formed by hydraulic pressure into pipes which are used in plumbing and for covering electric cables. On account of its very slow interaction with most substances, sheet lead is used in chemical factories, for example, to line sulphuric-acid chambers. An alloy containing 0.5 per cent of arsenic is used in making small shot and shrapnel bullets. Type-metal contains 20–25 per cent of antimony (*q.v.*), and expands on solidifying, giving a perfect reproduction of the mold. In both cases greater hardness (*cf.* p. 644) is secured by the addition of the foreign metal. Solder contains 50 per cent of tin and, being a solution, melts at a low temperature, and can be applied to solid lead without melting the latter.

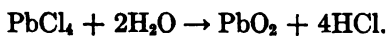
Lead oxidizes very superficially in the air. The suboxide  $\text{Pb}_2\text{O}$  is supposed to be first formed. The final covering is a basic carbonate. Contact with hard waters confers upon lead a similar coating composed of the carbonate and the sulphate. These deposits, being insoluble and strongly adherent, enclose the metal and protect the water from contamination with lead compounds. Pure rain-water, however, since it has no hardness, but contains oxygen in solution, gives the hydroxide  $\text{Pb}(\text{OH})_2$ , which is noticeably soluble. Hence lead pipes can safely be used only with somewhat hard water. When heated in the air, lead gives the monoxide  $\text{PbO}$  or minium  $\text{Pb}_3\text{O}_4$ , the latter at lower temperatures.

The metal displaces hydrogen from hydrochloric acid very slowly. It is hardly affected by concentrated sulphuric acid (*cf.* p. 436). Nitric acid attacks it readily, giving lead nitrate and oxides of nitrogen (p. 535).

**Chlorides and Iodide of Lead.** — Plumbic chloride  $\text{PbCl}_4$  is precipitated when a soluble chloride is added to a solution of a soluble

lead salt. It is slightly soluble in water (1.5 : 100) at 18°, and much more so at 100°. In the saturated solution at 25° about 50 per cent of the lead is in the form  $\text{Pb}^{++}$ , 44 per cent as  $\text{PbCl}^+$ , and 6 per cent as  $\text{PbCl}_2$  (cf. p. 439).

**Lead tetrachloride**  $\text{PbCl}_4$  is a solid at  $-15^\circ$ , and loses chlorine at room temperature. It is made by passing chlorine into plumbic chloride suspended in hydrochloric acid. The solution contains  $\text{H}_2\text{PbCl}_6$ . Ammonium chloride is added and ammonium chloroplumbate  $(\text{NH}_4)_2\text{PbCl}_6$ , analogous to pink-salt (p. 826), crystallizes out. When this is thrown into cold, concentrated sulphuric acid, an oil,  $\text{PbCl}_4$ , settles to the bottom. The oil fumes in the air and, in general, closely resembles stannic chloride  $\text{SnCl}_4$ . With little water, it slowly deposits  $\text{PbCl}_2$  and gives off chlorine. With much water, it is quickly hydrolyzed, and lead dioxide is thrown down:



**Lead iodide**  $\text{PbI}_2$  (yellow) is formed by precipitation. It crystallizes in yellow scales from solution in hot water.

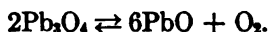
Plumbic chloride and iodide are both more soluble in acids or salts with a common negative ion than they are in water, and form soluble, but somewhat unstable, complex salts.

**Oxides and Hydroxides.** — There are five different oxides of lead,  $\text{Pb}_2\text{O}$ ,  $\text{PbO}$ ,  $\text{Pb}_2\text{O}_4$ ,  $\text{Pb}_2\text{O}_3$ , and  $\text{PbO}_2$ . The **suboxide**  $\text{Pb}_2\text{O}$  is a dark-gray powder, formed by gently heating the oxalate. **Plumbic oxide**, or lead monoxide  $\text{PbO}$ , is made by cupellation (p. 749) of lead, and the solidified, crystalline mass of yellowish-red color is sold as **litharge**. The yellow, powdery form is called **massicot**, and may be obtained by heating the nitrate or carbonate. All the other oxides yield this one when they are heated above  $600^\circ$  in the air. Plumbic oxide takes up carbon dioxide from the air, and therefore usually contains a basic carbonate. It dissolves in warm sodium hydroxide solution, giving a plumbite  $\text{Na}_2\text{PbO}_2$ ; a saturated solution redeposits part of the oxide in crystalline form when it cools. The oxide is used in making glass and enamels, and for preparing salts of lead. With glycerine, it gives a cement for glass or stone.

**Plumbic hydroxide**  $\text{Pb}(\text{OH})_2$  is formed by precipitation. It gives up water in three stages with different aqueous tensions (cf. p. 654), the products in the order of decreasing tension being  $\text{Pb}(\text{OH})_2$ ,  $\text{Pb}_2\text{O}(\text{OH})_2$ ,  $\text{Pb}_2\text{O}_2(\text{OH})_2$ . These substances, as will be seen, are equivalent in composition to  $\text{PbO}, \text{H}_2\text{O}$ ,  $2\text{PbO}, \text{H}_2\text{O}$ , and  $3\text{PbO}, \text{H}_2\text{O}$ ,

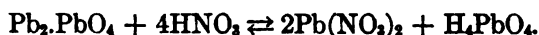
respectively. The hydroxide is observably soluble in water, and gives a solution with a faintly alkaline reaction. With acids it forms salts of lead. It interacts also with potassium and sodium hydroxides to form the soluble **plumbites**, like **sodium plumbite**  $\text{Na}_2\text{PbO}_2$ .

**Minium**, or **red lead**,  $\text{Pb}_3\text{O}_4$ , gives off oxygen when heated:



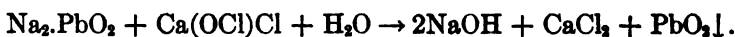
The dissociation pressure varies with the temperature:  $445^\circ$ , 5 mm.;  $500^\circ$ , 60 mm.;  $555^\circ$ , 183 mm.;  $636^\circ$ , 763 mm. Since the partial pressure of oxygen in the air is 150 mm., the substance decomposes at about  $550^\circ$ . It can be formed in air by reversal of the action represented above, but only below this temperature, namely at  $470$ – $480^\circ$  (cf. p. 301). In pure oxygen of one atmosphere pressure it could be formed at  $600^\circ$ , but not at  $650^\circ$ . On account of unequal heating during manufacture, commercial red lead is never fully oxidized, and always contains litharge. Conversely, commercial litharge usually contains a little minium.

Minium, when heated with warm, dilute nitric acid, is decomposed, and leaves lead dioxide as an insoluble powder. Two-thirds of the lead is basic and one-third acidic. Minium is therefore lead orthoplumbate (see below):



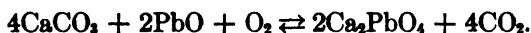
The double decomposition as a salt that it thus undergoes is followed by dehydration of the plumbic acid, which is unstable:  $\text{H}_4\text{PbO}_4 \rightarrow \text{PbO}_2 + 2\text{H}_2\text{O}$ , and the dioxide remains. Red lead is **used** in making flint glass and, when mixed with oil, gives a red paint which is specially applicable to iron-work (cf. p. 781).

**Lead dioxide**  $\text{PbO}_2$  may be obtained as described above in the form of a brown powder. Unlike most oxides, it is a conductor of electricity. It is usually made by adding bleaching powder to an alkaline solution of plumbic hydroxide:



In this action we may regard the free lead hydroxide, formed by hydrolysis of the plumbite, as being oxidized by the bleaching powder. This dioxide is an active oxidizing agent. It interacts with, and sets fire to, a stream of hydrogen sulphide, and it liberates chlorine from hydrochloric acid. With acids it gives no hydrogen peroxide, and is not a peroxidate (p. 321). Lead dioxide interacts with potassium and sodium hydroxides, giving soluble **plumbates**. These are derived

from metaplumbic acid. The potassium salt  $K_2PbO_3 \cdot 3H_2O$  is analogous to the metastannate  $K_2SnO_3 \cdot 3H_2O$  (p. 826). A mixture of calcium carbonate and lead monoxide absorbs oxygen when heated in a stream of air, and the yellowish-red calcium orthoplumbate is formed:



The action is reversible, and is at the basis of Kassner's plan for manufacturing oxygen from the air.

**Lead Nitrate  $Pb(NO_3)_2$ .** — This salt may be made by treating lead, lead monoxide, or lead carbonate with nitric acid. It forms white, anhydrous octahedra. The nitrate and acetate (see below) are the salts of lead which, because of their solubility, are most commonly used. The solubility of the nitrate is, 48 parts in 100 at  $10^\circ$ , and 153 parts at  $100^\circ$ . Since the solubility increases with rise in temperature, the process of solution is accompanied by absorption of heat (p. 305). On account of hydrolysis, the solution is acid in reaction.

**Lead Carbonate  $PbCO_3$ .** — This compound is found in nature in rhombic crystals, isomorphous with those of aragonite. It may be formed as a precipitate by adding a soluble bicarbonate to lead nitrate solution. With normal sodium carbonate, a basic carbonate  $Pb_3(OH)_2(CO_3)_2$  is deposited. This basic salt is identical with **white lead**, which, on account of its superior opacity, has better covering power than zinc-white (p. 770) or permanent white (p. 730). The substance is manufactured in various ways, all of which involve the oxidation of the lead by the air, the formation of a basic acetate by the interaction of vinegar or acetic acid with the oxide, and the subsequent decomposition of the salt by carbon dioxide. The best quality is obtained by the Dutch method. In this, gratings of cast lead ("buckles") are placed above a shallow layer of vinegar in small pots. These pots are buried in manure, which by its decomposition furnishes the carbon dioxide and the necessary warmth. The gratings are gradually converted into a white mass of the basic carbonate. The vapor of acetic acid arising from the vinegar may be regarded as a catalytic agent (cf. p. 436), since it is used over and over again. White lead is made also by blowing melted lead into dust by means of steam, beating the powder with air and water until it is converted into the hydrated monoxide, and treating the product with carbon dioxide and vinegar.

**Lead Acetate**  $Pb(CO_2CH_3)_2 \cdot 3H_2O$ . — This salt is made by the action of acetic acid on litharge. It is easily soluble in water and, from the sweet taste of the solution, is named *sugar of lead* (used in medicine). The basic salt  $Pb(OH)(CO_2CH_3)$  is formed by boiling a solution of lead acetate with excess of litharge. Unlike most basic salts, this one is soluble in water, and its solution has a faintly alkaline reaction.

**Lead Sulphate**  $PbSO_4$ . — The sulphate occurs in nature as anglesite, and is isomorphous with heavy spar. Being insoluble in water, it is easily obtained by precipitation. It is slightly soluble in concentrated sulphuric acid (p. 436). It is attacked to a noticeable extent by nitric acid, since this acid is more active than is sulphuric acid (cf. p. 367). It also interacts with concentrated sodium hydroxide solution, on account of the removal of the  $Pb^{++}$  ions which are a factor in its solubility product and their passage into the  $PbO_2^-$  anion of sodium plumbite (cf. p. 832). Finally, it dissolves easily in ammonium tartrate, since lead enters into the complex anion of the tartrates in the same way as does copper (cf. p. 744). Barium sulphate, which is of the same order of insolubility as lead sulphate, is somewhat affected by nitric acid, but not by sodium hydroxide or by tartrates. The element barium lacks both the characteristics which lead here exhibits.

**Lead Sulphide**  $PbS$ . — Natural lead sulphide (galena) is black, and its crystals have a silvery luster. The precipitated salt is black and amorphous. It is more easily attacked by active acids than is mercuric sulphide (cf. p. 774). Concentrated nitric acid, being an oxidizing agent as well as an acid, interacts with it readily.

**The Storage Battery.** — In the ordinary lead accumulator the plates consist of leaden gratings. The openings are filled with finely divided lead in one plate and with lead dioxide in the other. These, and the dilute sulphuric acid in the cell, are the active substances when the cell is charged. When the battery is used, the  $SO_4^-$  ions migrate towards the plates filled with the lead (Fig. 159), and convert this into a mass of the insoluble lead sulphate:  $SO_4^- + Pb \rightarrow PbSO_4 + 2e^-$ . These plates receive the negative charges. Simultaneously, the  $H^+$  ions move towards the other plates and these reduce to monoxide the lead dioxide with which they are filled:



These plates acquire positive charges and, by interaction of the lead monoxide with the sulphuric acid, become filled, like the negative plates, with lead sulphate. During the discharge, much sulphuric acid is thus removed from the cell fluid, and the approaching exhaustion of the cells can thus be ascertained by measuring the specific gravity of the fluid. The E.M.F. of the current is a little over 2 volts.

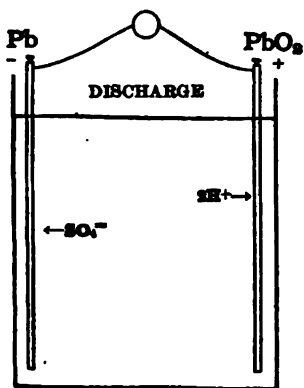


FIG. 159.

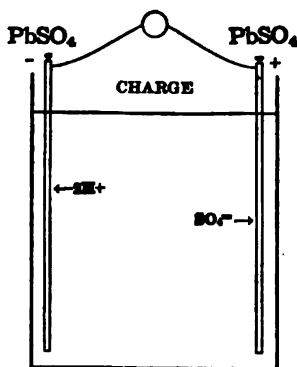
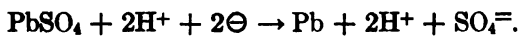


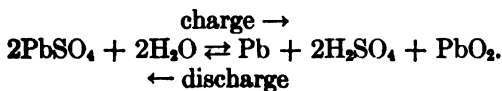
FIG. 160.

The charging is done by passing a current through the cell, in the opposite direction to the one which it yields (Fig. 160). The  $H^+$  ions are attracted to the negative plate and an equivalent number of  $SO_4^{=}$  ions are formed, so that only lead remains:



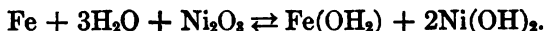
Simultaneously, the  $SO_4^{=}$  is attracted by the positive plate and, with the lead sulphate there present, forms lead persulphate:  $SO_4^{=} + PbSO_4 + 2\ominus \rightarrow Pb(SO_4)_2$ . The persulphate, being a salt of quad-valent lead, is at once hydrolyzed and the filling of this plate is thus changed into lead dioxide:  $Pb(SO_4)_2 + 2H_2O \rightarrow PbO_2 + 2H_2SO_4$ . Both plates are thus brought back to the condition in which they were before the discharge.

The last set of changes consumes energy, while the first set liberates energy. Both may be stated in a single equation:





In the **Edison cell**, when charged, one plate is of iron and the other contains nickelic oxide  $\text{Ni}_2\text{O}_3$ . The cell liquid is a solution of potassium hydroxide. When the cell operates, the nickelic oxide is reduced to  $\text{Ni}(\text{OH})_2$  and the iron is oxidized to  $\text{Fe}(\text{OH})_2$ , an action which delivers energy:



When the cell is charged, the nickel is reoxidized and the iron reduced.

**Paints.** — A paint usually contains three ingredients:

1. **The oil** hardens to a tough resin, being oxidized by the air ("dries"), and adheres firmly to the surface being painted.

2. **The body** is a fine powder which makes the paint opaque. Since the powder does not shrink, it also "fills" the paint and prevents the formation of minute pores which otherwise would appear in the oil after drying. White lead (p. 833) is a common material for the body, but zinc oxide, lithopone (p. 730) and other substances are used.

3. Except in the case of white paint, a **pigment** is added. Various oxides, such as minium, colored salts, and lakes (p. 820) are used as coloring matters.

The oil does not "dry" by evaporation but gives a resin by oxidation. Linseed oil and hemp oil are commonly used. They contain glyceryl esters (p. 618) of *unsaturated* acids, such as that of linoleic acid ( $\text{C}_3\text{H}_5(\text{CO}_2\text{C}_{17}\text{H}_{31})_2$ ), which contains four units of hydrogen less than stearic acid. The unsaturated part of the molecule takes up the oxygen. By previously boiling the oil with manganese dioxide and other oxides, it is rendered more active, and "dries" more quickly.

Plumbers use a cement made of minium and linseed oil, in which the former oxidizes the latter, without access of air being necessary.

**Analytical Reactions of Lead Compounds.** — Hydrogen sulphide precipitates the black sulphide, even when dilute acids are present. Sulphuric acid throws down the sulphate. Potassium hydroxide gives the white hydroxide, which interacts in excess to form the plumbite. Potassium chromate or dichromate (*q.v.*) gives a yellow precipitate of lead chromate  $\text{PbCrO}_4$ , which is used as a pigment under the name of "chrome-yellow."

## TITANIUM, ZIRCONIUM, CERIUM, THORIUM

The metals on the left side of the fifth column of the periodic table are all quadrivalent, although compounds in which a lower valence appears are numerous in this family. The first two are feebly base-forming as well as feebly acid-forming; the last two are base-forming exclusively.

**Titanium** occurs in rutile  $\text{TiTiO}_4$ . Derived from it are a number of titanates of the form  $\text{K}_2\text{TiO}_3$ , titanitic iron ore (menaccanite) being ferrous titanate  $\text{FeTiO}_3$ .

**Zirconium** is found in zircon, the orthosilicate of zirconium  $\text{ZrSiO}_4$ , which occurs in square prismatic crystals isomorphous with rutile, cassiterite ( $\text{SnSnO}_4$ ), pyrolusite ( $\text{MnMnO}_4$ ), and thorite ( $\text{ThSiO}_4$ ). The oxide was used at one time in making the incandescent substance in some forms of gas lamps.

**Cerium** occurs chiefly in cerite  $[\text{Ce}, \text{La}, \text{Nd}, \text{Pr}]\text{SiO}_4 \cdot \text{H}_2\text{O}$  (cf. p. 808). The particles of an alloy of cerium (70 per cent) and iron (30 per cent), when torn off by a file, catch fire in the air. This fact is utilized in making **gas-lighters** and cigar-lighters.

**Thorium** is found in thorite  $\text{ThSiO}_4$  but most of the supply comes from monazite sand. The nitrate  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  is used in making Welsbach incandescent mantles (cf. Flame, p. 596). The mantle of knitted cotton is dipped in a solution of this salt along with one per cent of cerium nitrate  $\text{Ce}(\text{NO}_3)_4$ , and is then ignited. The oxides  $\text{ThO}_2$  (thoria) and  $\text{CeO}_2$  (ceria), which remain, form a fairly coherent mass. Thorium and its compounds are radioactive (see Radium).

**Exercises.**—1. In what order should you place the elements dealt with in this chapter, beginning with the least metallic, and ending with the most metallic (p. 645)?

2. Construct equations showing, (a) the interaction of tin and concentrated sulphuric acid, (b) of water and stannous chloride, (c) of chlorauric acid and stannous chloride (p. 825), (d) of oxygen and stannous chloride in acid solution, (e) the decomposition of lead oxalate (p. 831), (f) the interaction of lead monoxide and acetic acid, (g) and of lead monoxide and lead acetate.

3. To which class of ionic actions (pp. 402–406) do the reductions by stannous chloride belong?

4. What interactions probably occur when lead dioxide liberates chlorine from hydrochloric acid?

5. How should you set about preparing, (a) lead oxalate (insoluble), (b) lead chlorate (soluble)?

6. Should the formula of the sulphate of quadrivalent-lead be written  $\text{Pb}(\text{SO}_4)_2$  or  $\text{PbS}_2\text{O}_8$ , and is it related to persulphuric acid  $\text{H}_2\text{S}_2\text{O}_8$ ?

7. Describe in terms of the categories used in connection with the phase rule (p. 705) the system furnished by minium at  $500^\circ$ .

8. Construct equations for the formation of white lead by the Dutch process, showing, (1) the formation of the basic acetate by the action of oxygen, water, and acetic acid vapor, and (2) the action of carbonic acid on the product.

## CHAPTER XLI

### ARSENIC, ANTIMONY, BISMUTH

THIS family is closely related to the elements phosphorus and nitrogen, which precede it in the same column of the periodic table. In reading this chapter, therefore, constant reference should be made to the chemistry of the corresponding compounds of phosphorus. For a general comparison of the elements **arsenic** (As, at. wt. 75), **antimony** (Sb, at. wt. 120.2), and **bismuth** (Bi, at. wt. 208) with each other, and with the two already disposed of, see p. 850. It is sufficient here to say that arsenic is mainly an acid-forming element, and is therefore non-metallic, while antimony is both acid-forming and base-forming, and bismuth is base-forming. Each of the three elements gives a set of compounds in which it is trivalent, and another in which it is quinquivalent. None of the elements, when free, displaces hydrogen from dilute acids.

#### ARSENIC As

**The Chemical Relations of the Element.** — Arsenic forms a compound with hydrogen  $\text{AsH}_3$ . It gives several halogen derivatives of the type  $\text{AsX}_3$  which are completely hydrolyzed by water. Its oxides and hydroxides are acidic. Sulphates, nitrates, carbonates, and other salts of arsenic are not formed. The complex sulphides are important. The soluble compounds of arsenic are all highly poisonous.

In many natural sulphides, such as pyrite  $\text{FeS}_2$  and zinc-blende  $\text{ZnS}$ , a part of the sulphur is replaced by arsenic, which must here be playing the part of a bivalent element. When much arsenic is present, the formulæ are written:  $\text{Fe}[\text{S},\text{As}]_2$  and  $\text{Zn}[\text{S},\text{As}]$ .

**Occurrence and Preparation.** — Arsenic is found free in nature. It occurs also in combination with many metals, particularly in arsenical pyrite (mispickel)  $\text{FeAsS}$ . Two sulphides, orpiment  $\text{As}_2\text{S}_3$  and realgar  $\text{As}_2\text{S}_2$ , and white arsenic  $\text{As}_2\text{O}_3$ , are less common.

The element is obtained either from the native material or by heating arsenical pyrites:  $\text{FeAsS} \rightarrow \text{FeS} + \text{As}$ . During the roasting

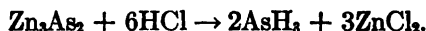
of the sulphur ores of metals, arsenic trioxide is formed by the oxidation of the arsenic so frequently present, and collects as a dust in the flues. The supply is greatly in excess of the demand.

**Physical Properties.** — The free element is steel-gray in color, metallic in appearance, and crystalline in form. When the vapor is suddenly cooled, however, a yellow, less stable variety is obtained, which is soluble in carbon disulphide, is phosphorescent in the air, and in other ways resembles white phosphorus.

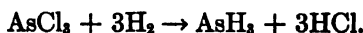
Elementary arsenic gives off vapor at  $180^{\circ}$ , and above  $600^{\circ}$  acquires a vapor pressure of 760 mm. The density of the vapor measured at  $644^{\circ}$  gives 308.4 as the weight of the G.M.V. (22.4 liters at  $0^{\circ}$  and 760 mm.). The weight combining with one unit (35.46 g.) of chlorine is 25 g., and three times this amount, or 75 g., is the smallest weight found in the G.M.V. of any volatile compound of arsenic, and is therefore accepted as the atomic weight. Since 308.4 is equal approximately to  $4 \times 75 (= 300)$ , the formula of the vapor of the simple substance at  $644^{\circ}$  is  $As_4$ . At  $1700^{\circ}$  the formula is  $As_2$ .

**Chemical Properties.** — The free element burns in the air, producing clouds of the solid trioxide  $As_2O_3$ . It unites directly with the halogens, with sulphur, and with many of the metals. When boiled with nitric acid, chlorine water, and other powerful oxidizing agents, it is oxidized in the same way as is phosphorus, and yields arsenic acid  $H_3AsO_4$ .

**Arsine  $AsH_3$ .** — This substance corresponds in composition to ammonia and phosphine, and some of the ways in which it may be formed are analogous to those used in the case of these substances. Thus, when arsenic and zinc are melted together in the proportions to form **zinc arsenide**  $Zn_3As_2$ , and the product is treated with dilute hydrochloric acid, the result is similar to the action of water or dilute acids upon calcium phosphide. Arsine is evolved as a gas:



Arsine (arsenuretted hydrogen) is formed also by the action of active hydrogen (cf. p. 543) upon soluble compounds of arsenic, such as arsenious chloride  $AsCl_3$  or arsenic acid. When a solution of one of these substances is added to zinc and hydrochloric acid in a generating flask, arsine is formed:



This method, naturally, does not furnish pure arsine, for free hydrogen predominates in the gas. Pure arsine may be secured by leading the mixture with hydrogen through a U-tube immersed in liquid air. The arsine (b.-p.  $-55^{\circ}$ ) condenses as a colorless liquid (m.-p.  $-119^{\circ}$ ).

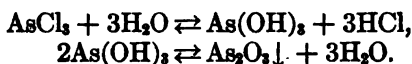
Arsine burns with a bluish flame, producing water and clouds of arsenic trioxide:  $2\text{AsH}_3 + 3\text{O}_2 \rightarrow 3\text{H}_2\text{O} + \text{As}_2\text{O}_3$ . The combustion of hydrogen containing arsine produces the same substances. Since arsine, when heated, is readily dissociated into its constituents (*cf.* p. 416), the vapor of free arsenic is present in the interior of the hydrogen flame. This arsenic may be condensed in the form of a metallic-looking, brownish stain by interposition of a cold vessel of white porcelain. Even when only a trace of the compound of arsenic has been added to the materials in the generator, the stain which is produced is very conspicuous. This behavior thus furnishes us with an exceedingly delicate test — **Marsh's test** — for the presence of arsenic in any soluble form of combination. The compounds of antimony alone show a similar phenomenon (see Stibine). In carrying out the test, a tube of hard glass is attached to the generator, and is heated, by means of a Bunsen flame, at a point near to the flask. With this arrangement the arsenic is deposited in the form of a dark, lustrous ring just beyond the heated part. Zinc of special purity must be employed for generating the hydrogen, as all common specimens of the metal contain a sufficient amount of arsenic to give the metallic film without any actual addition of an arsenic compound, and a blank experiment must be run, with other portions of the same reagents, to guard against the possibility of its coming from any of them. Arsenic is more easily detected than any other poison which can be used in small amounts.

Arsine is exceedingly **poisonous**, the breathing of small amounts producing fatal effects. It differs from ammonia more markedly than does phosphine, for it is not only without action on water and on acids, but does not unite directly even with the halides of hydrogen.

**Halides of Arsenic.** — The halides include a liquid **trifluoride**  $\text{AsF}_3$ , a **pentafluoride**, which is obtained only as a double compound with potassium fluoride, a liquid **trichloride**  $\text{AsCl}_3$ , a solid **tribromide**  $\text{AsBr}_3$ , and a solid **tri-iodide**  $\text{AsI}_3$ .

The **trichloride**,  $\text{AsCl}_3$ , which is prepared by passing chlorine gas into a vessel containing arsenic, is easily formed as the result of a vigorous action. It is a colorless liquid, boiling at  $130^{\circ}$ . When mixed with water it is at once converted into the white, almost insolu-

ble trioxide. The action is presumably similar to that of water upon the corresponding compound of phosphorus (p. 210), but the arsenious acid for the most part loses water and forms the insoluble anhydride:



This action, however, differs markedly from the other in that it is **reversible**, and arsenic trioxide interacts with aqueous hydrochloric acid, giving a solution of arsenious chloride. When this solution is boiled, the volatility of the arsenious chloride causes it to be carried over with the hydrochloric acid (b.-p.  $110^\circ$ , cf. p. 563), and this method of separating arsenic from other substances is used in chemical analysis.

**Oxides of Arsenic.**—**Arsenic trioxide**  $\text{As}_2\text{O}_3$  is produced by burning arsenic in the air and during the roasting of arsenical ores (p. 840), and is known as “white arsenic” or simply “arsenic.” It is purified for commercial purposes by subliming the flue-dust in cylindrical pots. The pure trioxide is deposited in the glassy form in the upper part of the vessel. It passes slowly from this amorphous condition into the common crystalline variety. Its vapor density indicates that it possesses the molecular weight  $\text{As}_4\text{O}_6$ , but the simpler formula expresses its chemical properties sufficiently well.

When treated with water, the trioxide dissolves to a very slight extent (1.2 : 100 at  $2^\circ$ ), forming arsenious acid, by reversal of the second of the equations given above. As usual, the less stable, amorphous variety is the more soluble. In boiling water the solubility is much greater (11.5 : 100), but a condition of equilibrium is reached very slowly. With concentrated sulphuric acid the trioxide forms a sulphate of rather complex composition, indicating that it has basic properties, but this sulphate is decomposed into the oxide and sulphuric acid when treated with water. When heated in a tube with carbon, this oxide is reduced, and the free element, being volatile, is deposited upon the cold part of the tube just above the flame. It is an active poison, since it gradually passes into solution, forming arsenious acid. The fatal dose is 0.06–0.18 g. (1–3 grains), but “arsenic eaters” become tolerant of it and can take four times as much without evil effects. It is contained in Fowler’s solution, which is used as a heart tonic.

The **pentoxide**  $\text{As}_2\text{O}_5$  is a white crystalline substance, formed by

heating arsenic acid:  $2\text{H}_3\text{AsO}_4 \rightarrow \text{As}_2\text{O}_5 + 3\text{H}_2\text{O}$ . When raised to a higher temperature, it loses a part of its oxygen, leaving the trioxide. In consequence of this instability, it cannot be formed by direct union of oxygen with the trioxide, as can phosphorus pentoxide.

**Acids of Arsenic.**—When elementary arsenic or arsenious oxide is treated with concentrated nitric acid, or with chlorine and water, **orthoarsenic acid**  $\text{H}_3\text{AsO}_4$  is produced. The substance crystallizes as a deliquescent white solid  $2\text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$ . **Salts** of this acid, and of pyroarsenic acid  $\text{H}_4\text{As}_2\text{O}_7$  and metarsenic acid  $\text{HAsO}_3$ , corresponding to the phosphoric acids (p. 557), are known. The two last acids, themselves, however, are not known as such. It has been shown by Menzies that, when the hemihydrate of orthoarsenic acid is dried at  $100^\circ$ , the only acid obtainable has the composition  $\text{H}_3\text{As}_2\text{O}_{10}$  ( $= 5\text{H}_2\text{O} \cdot 3\text{As}_2\text{O}_5$ ). When this acid is heated more strongly, it loses water, leaving the pentoxide  $\text{As}_2\text{O}_5$ . With the phosphoric acids, the final elimination of all the water by simple heating is impossible. The chocolate-brown **silver orthoarsenate**  $\text{Ag}_3\text{AsO}_4$  and the white  $\text{MgNH}_4\text{AsO}_4$ , like the corresponding phosphates, are insoluble in water.

**Arsenious acid**  $\text{H}_3\text{AsO}_3$ , like sulphurous and carbonic acids, loses water, and yields the anhydride, arsenic trioxide, when the attempt is made to obtain it from the aqueous solution. The **potassium** and **sodium arsenites**,  $\text{K}_2\text{AsO}_3$  and  $\text{Na}_2\text{AsO}_3$ , are made by treating arsenic trioxide with caustic alkalies, and are much hydrolyzed by water. The arsenites of the heavy metals are insoluble, and can be made by precipitation. Paris green and Scheele's green (p. 745) are arsenites of copper. The poisonous effects of wall-paper colored with these compounds seem to be due to volatile organic derivatives of arsine which are formed by the action of a mold. In cases of poisoning by white arsenic, freshly precipitated ferric hydroxide or magnesium hydroxide is administered, since by interaction with the arsenious acid they form insoluble arsenites. The salts of arsenious acid are readily oxidized, passing into arsenates. The action of a standard solution of iodine upon sodium arsenite, for example, is used in volumetric analysis:



**Sulphides of Arsenic.**—Three sulphides of arsenic are known,  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{S}_5$ ,  $\text{As}_4\text{S}_6$ . The first, **arsenic pentasulphide**  $\text{As}_2\text{S}_5$ , is obtained as a yellow powder by decomposition of the sulpharsenates

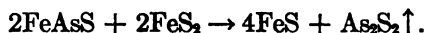


(see below), and by leading hydrogen sulphide into a solution of arsenic acid in *concentrated* hydrochloric acid. The latter action shows that the ion  $\text{As}^{++++}$ , derived from  $\text{AsCl}_5$ , is present in the solution.

**Arsenious sulphide**  $\text{As}_2\text{S}_3$  occurs in nature as orpiment, and was formerly used as a yellow pigment (*auripigmentum*). The word arsenic is derived from the Greek name for this mineral (*ἀρσενικόν*). It is obtained as a citron-yellow precipitate when hydrogen sulphide is led into an aqueous solution of arsenious chloride.

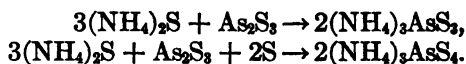
When hydrogen sulphide is led into an aqueous solution of arsenious acid, the sulphide is formed, but remains in **colloidal suspension**. It is a negatively charged colloid (p. 622), a small amount of  $\text{H}^+$  ion in the liquid rendering the whole electrically neutral. It is coagulated by adding solutions of salts, lower concentrations being sufficient the higher the valence of the positive ion of the salt (0.05 Molar  $\text{KCl}$ , 0.0007  $M$   $\text{BaCl}_2$ , 0.00009  $M$   $\text{AlCl}_3$ ).

**Realgar**  $\text{As}_2\text{S}_2$  is a natural sulphide of orange-red color, and is also manufactured by subliming a mixture of arsenical pyrite and pyrite:



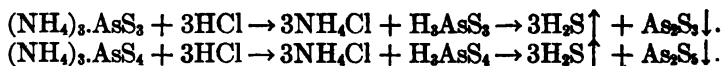
It burns in oxygen, forming arsenious oxide and sulphur dioxide, and is mixed with potassium nitrate and sulphur to make "Bengal lights."

**Sulpharsenites and Sulpharsenates.** — The sulphides of arsenic interact with solutions of alkali sulphides after the manner of the sulphides of tin (p. 828), giving soluble, complex sulphides. Arsenious sulphide with colorless ammonium sulphide gives ammonium sulpharsenite, and with the yellow sulphide gives ammonium sulpharsenate:



Proustite (p. 749) is a natural sulpharsenite of silver. The formation of these soluble compounds is used in analysis (*cf.* p. 783).

These salts are decomposed by acids, and give free sulpharsenious or sulpharsenic acid:

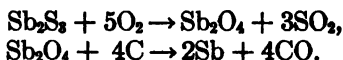


These sulpho-acids, however, at once break up, giving hydrogen sulphide as a gas, and the sulphides of arsenic as yellow precipitates.

## ANTIMONY Sb

**The Chemical Relations of the Element.** — Antimony resembles arsenic in forming a hydride  $\text{SbH}_3$ , and halides of the forms  $\text{SbX}_3$  and  $\text{SbX}_5$ . The halides are partially hydrolyzed by water with ease, but complete hydrolysis is difficult to accomplish with cold water. The oxide  $\text{Sb}_2\text{O}_3$  is basic as well as feebly acidic (amphoteric), and the oxide  $\text{Sb}_2\text{O}_5$  is acidic. The compositions of the compounds are similar to those of the compounds of arsenic, but there are in addition salts, such as  $\text{Sb}_2(\text{SO}_4)_3$ , derived from the oxide  $\text{Sb}_2\text{O}_3$ . The element gives complex sulphides like those of arsenic.

**Occurrence and Preparation.** — Antimony occurs free in nature. The chief supply, however, is furnished by the black trisulphide  $\text{Sb}_2\text{S}_3$ , stibnite, which is found in Hungary and Japan, and forms shining, prismatic crystals of the rhombic system. Native stibnite is roasted in the air in order to remove the sulphur, and the white oxide which remains is mixed with carbon and reduced by strong heat:



**Properties.** — Antimony is a white, crystalline metal, melting at  $630^\circ$  (b.-p.  $1300^\circ$ ). It is brittle, and easily powdered. Its vapor at  $1640^\circ$  has a density corresponding to the formula  $\text{Sb}_2$ , while at lower temperatures  $\text{Sb}_4$  is present. It is used in making alloys such as type-metal, stereotype-metal, and britannia metal (*q.v.*). The alloys of antimony expand during solidification, and therefore give exceptionally sharp castings.

**Babbitt's Metal** (Sb 3, Zn 69, As 4, Pb 5, Sn 19), and other **anti-friction alloys** used in lining bearings, contain antimony along with zinc, copper, and other metals. Molten mixtures of metals (alloys), when solidifying, do not always form a homogeneous, solid mass. In an anti-friction alloy, what is wanted is a mass, in general soft, but containing hard particles. The latter bear most of the pressure, yet, as the alloy wears, *they are pressed into the softer matrix* so that a smooth surface is always presented. An alloy which has the opposite composition, that is, which gives a hard mass containing softer particles, develops heat by friction much more rapidly.

The element unites directly with the halogens. It does not rust, but when heated it burns in the air, forming the trioxide  $\text{Sb}_2\text{O}_3$  or a

higher oxide  $\text{Sb}_2\text{O}_4$ . When heated with nitric acid, it yields the trioxide and, with more difficulty, antimononic acid  $\text{H}_3\text{SbO}_4$ . When heated with concentrated sulphuric acid, it forms the sulphate  $\text{Sb}_2(\text{SO}_4)_3$ .

**Stibine  $\text{SbH}_3$ .** — The hydride of antimony  $\text{SbH}_3$  is formed by the action of zinc and hydrochloric acid on a soluble compound of antimony. By the action of dilute, cold hydrochloric acid on an alloy of antimony and magnesium (1 : 2), a mixture of hydrogen and stibine containing as much as 11.5 per cent (by volume) of the latter may be made. It is separated by cooling with liquid air (b.-p.  $-17^\circ$ , m.-p.  $-88^\circ$ ). It is more easily dissociated than is arsine, and forms a deposit of antimony when a porcelain vessel is held in the flame. The behavior is in all respects similar to that of arsine (p. 841).

The layers of arsenic or antimony obtained upon white porcelain in Marsh's test (p. 841) may be distinguished readily in several ways. The arsenic spots are brownish in color, lustrous, and volatile. The antimony spots are black, smoky-looking, and involatile at the temperature of the Bunsen flame. The arsenic spots dissolve in a fresh solution of bleaching powder, producing calcium chloride and arsenic acid, while those of antimony are unaffected. The arsenic spots are scarcely attacked by a solution of yellow ammonium sulphide, while those of antimony dissolve readily, forming an ammonium sulphantimoniate. Another distinction between arsine and stibine is found in their action upon a solution of nitrate of silver. Stibine precipitates a silver antimonide  $\text{Ag}_3\text{Sb}$ , and none of the antimony remains in the solution. Arsine, on the contrary, precipitates metallic silver, while arsenious acid remains in the solution.

**Antimony Halides.** — The halides include the trichloride, the pentachloride  $\text{SbCl}_5$ , a liquid (m.-p.  $-6^\circ$ , b.-p.  $140^\circ$ ), the tribromide  $\text{SbBr}_3$ , tri-iodide  $\text{SbI}_3$ , trifluoride  $\text{SbF}_3$ , and pentafluoride  $\text{SbF}_5$ .

**Antimony trichloride  $\text{SbCl}_3$**  is made by direct union of the elements. It forms large, soft crystals, and used to be named "butter of antimony (b.-p.  $223^\circ$ ).". When treated with little water, it forms a white, opaque, insoluble basic salt, antimony oxychloride:



With a large amount of water, a greater proportion of the chlorine is removed, and  $\text{Sb}_4\text{O}_5\text{Cl}_2$  ( $= 2\text{SbOCl}, \text{Sb}_2\text{O}_3$ ) remains. With boiling water the oxide is finally formed. The action is not complete as long

as hydrochloric acid is present. It may therefore be reversed, so that on addition of hydrochloric acid to the mixture, a clear solution of the trichloride is re-formed. If the concentration of the acid is once more reduced by dilution with water, the oxychloride is again precipitated.

The **pentachloride** is formed by leading chlorine over the trichloride. It is a liquid which fumes strongly in the air, being hydrolyzed by the moisture.

**Oxides of Antimony.** — Three oxides are known: antimony trioxide  $\text{Sb}_2\text{O}_3$ , antimony pentoxide  $\text{Sb}_2\text{O}_5$ , and an intermediate oxide  $\text{Sb}_2\text{O}_4$ . The **trioxide**  $\text{Sb}_2\text{O}_3$  is obtained by oxidizing antimony with nitric acid, or by combustion of antimony with a limited supply of oxygen. It is a white substance, insoluble in water. It is in the main a basic oxide, interacting with many acids to form salts of antimony. But it interacts also with alkalies, giving soluble **antimonites**. The **pentoxide**  $\text{Sb}_2\text{O}_5$  is a yellow, amorphous substance, obtained by heating antimoninic acid. It combines only with bases to form salts, and is therefore an acid-forming oxide exclusively. The **tetroxide**  $\text{Sb}_2\text{O}_4$  is formed by heating antimony or the trioxide in excess of oxygen. It is the most stable of the three oxides. It is neither acid- nor base-forming, and may be antimoniate of antimony ( $\text{SbSbO}_4$ ).

The hydrated trioxide  $\text{Sb}(\text{OH})_3$  may be obtained as a white precipitate by adding dilute sulphuric acid to tartar-emetic (see below). It is insoluble, and easily loses water, giving the trioxide.

**Salts of Antimony.** — The **nitrate**  $\text{Sb}(\text{NO}_3)_3$  and the **sulphate**  $\text{Sb}_2(\text{SO}_4)_3$  are made by the interaction of the trioxide with nitric and sulphuric acids. They are hydrolyzed by water, giving basic salts, such as  $(\text{SbO})_2\text{SO}_4$  ( $= \text{Sb}_2\text{O}_2\text{SO}_4$ ), which, like  $\text{SbOCl}$ , are derived from the hydroxide  $\text{SbO}(\text{OH})$ . When the trioxide is heated with a solution of potassium bitartrate  $\text{KHC}_4\text{H}_4\text{O}_6$ , a basic salt  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6, \frac{1}{2}\text{H}_2\text{O}$ , known as **tartar-emetic**, is formed. This is a white, crystalline substance which is soluble in water and is used in medicine. The univalent group  $\text{SbO}^+$  is known as **antimonyl**, and the above mentioned basic compounds are often called antimonyl sulphate, etc.

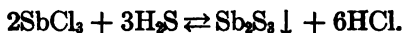
**Antimonic Acid.** — By vigorous oxidation of antimony with nitric acid, or by decomposing the pentachloride completely with water, a white, insoluble substance of the approximate composition  $\text{H}_5\text{SbO}_4$  is obtained. This substance interacts with caustic potash

and passes into solution. But the salts which have been made are pyro- and metantimonates. Thus, when antimony is fused with niter, **potassium metantimonate**  $\text{KSbO}_3$  is formed. When dissolved, this salt takes up water, and forms a solution of the acid pyroantimonate:



If this is added to a strong solution of a salt of sodium, a **sodium pyroantimonate**  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$  is thrown down. This compound, almost the only somewhat insoluble salt of sodium, is formed also by direct action of sodium hydroxide upon antimonious acid.

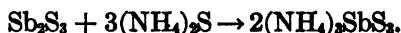
**Sulphides of Antimony.** — There are two sulphides, the trisulphide  $\text{Sb}_2\text{S}_3$  and the pentasulphide  $\text{Sb}_2\text{S}_5$ . The **trisulphide**  $\text{Sb}_2\text{S}_3$  is found in nature as the black, crystalline stibnite. By the action of hydrogen sulphide upon solutions of salts of antimony, the trisulphide is precipitated as an orange-red powder, which, however, after having been melted, assumes the appearance of stibnite:



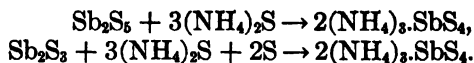
The antimony trisulphide is decomposed, and the above action is reversed, by concentrated hydrochloric acid. Like cadmium sulphide, this substance is formed only when the acid present is dilute.

The **pentasulphide**  $\text{Sb}_2\text{S}_5$  is obtained by the decomposition of sulphantimonates (see below). In appearance it resembles the trisulphide and, when heated, it decomposes very readily into this substance and free sulphur. It is used for vulcanizing rubber.

**Sulphantimonites and Sulphantimonates.** — The behavior of the sulphides of antimony towards solutions of the alkali sulphides is very similar to that of the sulphides of arsenic (p. 844). The trisulphide dissolves in colorless ammonium sulphide with difficulty, forming an unstable ammonium sulphantimonite:



With the pentasulphide, or with yellow ammonium sulphide, the action takes place more readily and ammonium sulphantimonate is formed:



The most familiar substance of this class is **Schlippe's salt**

$\text{Na}_2\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ . Pyrargyrite  $\text{Ag}_3\text{SbS}_3$  (p. 749) is a mineral sulphantimonite.

When acids are added to solutions of sulphantimonates, the sulphantimonic acid which is liberated decomposes, and antimony pentasulphide is thrown down (see under Arsenic, p. 844).

### BISMUTH Bi

**The Chemical Relations of the Element.** — Bismuth forms no compound with hydrogen. Its compounds with the halogens are of the form  $\text{BiX}_3$  and are hydrolyzed by water giving basic salts. The oxide  $\text{Bi}_2\text{O}_3$  is basic and, although an oxide  $\text{Bi}_2\text{O}_5$  is known, it is not acidic. Bismuth gives a carbonate, nitrate, sulphate, phosphate, and other salts, in all of which it acts as a trivalent element. It forms no soluble complex sulphides.

**Occurrence and Physical Properties.** — This element is found free in nature, and also to some extent as trioxide  $\text{Bi}_2\text{O}_3$  and trisulphide  $\text{Bi}_2\text{S}_3$ . It is a shining, brittle metal with a reddish tinge (m.-p.  $271^\circ$ ). Bismuth is one of the few substances (see water) which expand on solidifying, the crystals being lighter than the liquid at  $271^\circ$ . It is dimorphous, with a transition point (p. 412) at  $75^\circ$ . When converted into vapor, its density at  $1600\text{--}1700^\circ$  is somewhat less than that corresponding to the formula  $\text{Bi}_3$ .

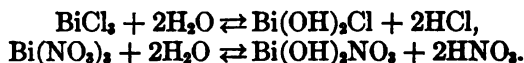
Mixtures of bismuth with other metals of low melting-point fuse at lower temperatures than do the separate metals. This is another illustration of the fact that a solution melts at a lower temperature than the pure solvent (p. 644). Thus, **Wood's metal**, containing bismuth (m.-p.  $271^\circ$ ) 4 parts, lead (m.-p.  $327^\circ$ ) 2 parts, tin (m.-p.  $232^\circ$ ) 1 part, and cadmium (m.-p.  $321^\circ$ ) 1 part, melts at  $60.5^\circ$ , considerably below the boiling-point of water. Similar alloys are used for safety plugs in steam-boilers and automatic sprinklers.

**Chemical Properties.** — Bismuth does not tarnish, but when heated strongly in the air it burns to form the trioxide. With the halogens it forms a **fluoride**  $\text{BiF}_3$ , a **chloride**  $\text{BiCl}_3$ , a **bromide**  $\text{BiBr}_3$ , and an **iodide**  $\text{BiI}_3$ . When the metal is treated with oxygen acids, or the trioxide with any acids, salts are produced.

**Oxides.** — In addition to the basic trioxide, which is a yellow powder obtained by direct oxidation of the metal or by ignition of the

nitrate, three other oxides are known —  $\text{BiO}$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{Bi}_2\text{O}_5$ . None of these, however, is either acid-forming, or base-forming.

**Salts of Bismuth.** — The salts of bismuth, when dissolved in water, like those of antimony, give insoluble basic salts, and the actions are reversible, the basic salts being redissolved by addition of an excess of the acid. In the case of the **chloride**  $\text{BiCl}_3 \cdot \text{H}_2\text{O}$  and the **nitrate**  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , the actions taking place are:



The former of these products, when dried, loses a molecule of water, giving the **oxychloride**  $\text{BiOCl}$ . The **oxynitrate** of bismuth is much used, for the treatment of some forms of indigestion, under the name "subnitrate of bismuth." It is often contained in face powders.

It will be seen that, although bismuth forms a colorless ion  $\text{Bi}^{+++}$ , and is in this respect a metal in the chemical sense of the term, yet, like many other metals, it is related to the non-metals inasmuch as its salts are at least partially hydrolyzed by water.

The brownish-black, insoluble **trisulphide**  $\text{Bi}_2\text{S}_3$ , may be obtained by direct union of the elements, or by precipitation with hydrogen sulphide. On addition of much acid the second of the above actions is reversed. This sulphide is not affected by solutions of ammonium sulphide or of potassium sulphide. It differs, therefore, markedly from the sulphides of arsenic and antimony in its behavior.

### THE FAMILY AS A WHOLE

When we compare the elements of this group, taking nitrogen as the first of the family, in spite of the fact that it is somewhat less closely related to the other members than they are to one another, we find an admirable illustration of the general principles which the periodic system presents.

The elements themselves change progressively in physical properties as the atomic weight increases. Nitrogen is a gas which with sufficient cooling yields a white solid, phosphorus a white, or a red solid, and arsenic, antimony, and bismuth are metallic in appearance. The first combines directly with hydrogen, the next three give hydrides indirectly, and the last does not unite with hydrogen at all. The hydride of nitrogen combines with water to form a base, while the other hydrides show no such tendency. Ammonia unites with

all acids, including those of the halogens, to form salts; phosphine with the hydrogen halides only; the others do not combine with acids at all. As regards their metallic properties, in the chemical sense, nitrogen and phosphorus do not by themselves form positive ions, and furnish us therefore with no salts whatever. Arsenic gives a trivalent positive ion, which is found in solutions of the halides only. It forms no normal sulphates, nitrates, or other salts. Antimony and bismuth both give trivalent positive ions. The sulphates, nitrates, etc., of antimony, however, are readily decomposed by water with precipitation of the hydroxide. The salts of bismuth, on the other hand, do not readily give the pure hydroxide with water, although they are easily hydrolyzed to basic salts.

The halogen compounds of nitrogen and phosphorus are completely hydrolyzed by water, and do not exist when any water is present, even when excess of the halogen acid is used. The halogen compounds of arsenic are completely hydrolyzed by cold water, but exist in solution in presence of excess of the acids. The halogen compounds of antimony and bismuth are incompletely hydrolyzed by cold water.

Each element gives a trioxide and a pentoxide. With nitrogen these are acid-forming, being the anhydrides of nitrous and nitric acids. With phosphorus the trioxide and the pentoxide are anhydrides of acids. With arsenic the trioxide is basic towards the halogen acids, and is the first example of a basic oxide which we encounter in this group. The pentoxide, however, is acid-forming. The trioxide of antimony is mainly base-forming, although it is feebly acid-forming also. The pentoxide is acid-forming. The trioxide of bismuth is base-forming exclusively, and the pentoxide has no derivatives.

These statements, which could easily be expanded, are sufficient to show that when the periodic law is borne in mind it furnishes valuable aid in systematizing the chemistry of a group like this.

#### *Analytical Reactions of Arsenic, Antimony, and Bismuth.*

— The ions which are most frequently encountered are  $\text{As}^{+++}$ ,  $\text{Sb}^{+++}$ ,  $\text{Bi}^{+++}$ ,  $\text{AsO}_4^{=}$ , and  $\text{AsO}_3^{=}$ . The first three, with hydrogen sulphide, give colored sulphides which are not affected by dilute acids. The sulphides of arsenic and antimony are separable from the sulphide of bismuth by solution in yellow ammonium sulphide. The ion of the arsenates  $\text{AsO}_4^{=}$  is identified by its interaction with salts of silver and the formation of  $\text{MgNH}_4\text{AsO}_4$ , while that of the arsenites



$\text{AsO}_3^{--}$  is recognized by its reducing power. Marsh's test (p. 841) enables us to recognize the presence of traces of compounds of arsenic and antimony. Oxygen compounds of arsenic, when heated with carbon, give a volatile, metallic-looking deposit of arsenic.

### VANADIUM, COLUMBIUM, TANTALUM

Of these elements, **vanadium** is less uncommon than the others. It is found in rather complex compounds. When these are heated with soda and sodium nitrate, **sodium vanadate**  $\text{NaVO}_3$  is formed, and can be extracted with water. Solid ammonium chloride is added to the solution, and ammonium metavanadate  $\text{NH}_4\text{VO}_3$ , which is less soluble in solutions of salts of ammonium (cf. p. 698) than in water, appears in the form of yellow crystals. When this salt is heated, **vanadic anhydride**  $\text{V}_2\text{O}_5$ , a yellowish-red powder, remains. This oxide interacts with bases giving vanadates, of which the most stable are the metavanadates. The element forms several **chlorides**, such as  $\text{VCl}_2$ ,  $\text{VCl}_3$ ,  $\text{VCl}_4$ ,  $\text{VOCl}_3$ , and five **oxides**,  $\text{V}_2\text{O}$ ,  $\text{VO}$ ,  $\text{V}_2\text{O}_3$ ,  $\text{VO}_2$ , and  $\text{V}_2\text{O}_5$ . The element has very feeble base-forming properties, and gives only a few, unstable salts. Ferrovandium, an alloy with iron, is used in making vanadium steel (*q.v.*).

**Columbium** (or niobium), first discovered and named by Hatchett (1801), and **tantalum** likewise possess feebly base-forming properties, their chief compounds being the columbates and tantalates.

**Exercises.**—1. How do you account for the fact that the molecular weight of arsenic at  $644^\circ$  is not exactly 300, and why is  $308.4 \div 4$  not accepted as the atomic weight?

2. What should you expect to be the interaction of arsine with concentrated nitric acid?

3. Formulate the series of changes involved in the solution of arsenic trioxide and the interaction of hydrochloric acid with the arsenious acid so formed (cf. p. 666).

4. What is the full significance of the fact that arsenic pentasulphide may be precipitated by hydrogen sulphide from a solution of arsenic acid in hydrochloric acid? Make the equation.

5. To what classes of chemical changes do the interactions of arsenious sulphide and antimony trisulphide with yellow ammonium sulphide belong?

6. Construct equations showing the interaction of, (a) concen-

trated sulphuric acid and antimony, (b) arsenic and bleaching-powder solution, (c) antimony and yellow ammonium sulphide, (d) silver nitrate and stibine, (e) silver nitrate and arsine, (f) concentrated nitric acid and antimony, (g) acids and ammonium orthosulphantimonate.

7. How should you set about making Schlippe's salt?

## CHAPTER XLII

### THE CHROMIUM FAMILY. RADIUM

THE chromium (Cr, at. wt. 52) family includes molybdenum (Mo, at. wt. 96), tungsten (W, at. wt. 184), and uranium (U, at. wt. 238.2), and occupies the left side of the seventh column of the periodic table, with the sulphur family on the right side.

*The Chemical Relations of the Family.*—The features which are common to the four elements are also those which affiliate them most closely with their neighbors on the right side of the column. They yield oxides of the forms  $\text{CrO}_3$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ , and  $\text{UO}_3$ , which, like  $\text{SO}_3$ , are acid anhydrides, and show the elements to be sexivalent. They give also acids of the form  $\text{H}_2\text{XO}_4$ , corresponding to sulphuric acid, and the salts resemble the sulphates. Thus, sodium chromate  $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$  is isomorphous with Glauber's salt (p. 690), and potassium chromate  $\text{K}_2\text{CrO}_4$  with potassium sulphate.

Aside from the chromates, the first element forms also two basic hydroxides  $\text{Cr}(\text{OH})_2$  and  $\text{Cr}(\text{OH})_3$ , from which the numerous chromous ( $\text{Cr}^{++}$ ) and chromic ( $\text{Cr}^{+++}$ ) salts are derived. Uranium forms a dioxide  $\text{UO}_2$ , to which correspond the uranous salts like  $\text{U}(\text{SO}_4)_2$ , but the most familiar salts of this metal are basic salts of the oxide  $\text{UO}_3$ , and have the form  $\text{UO}_2(\text{NO}_3)_2$ . Molybdenum and tungsten are not base-forming elements.

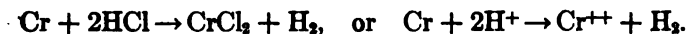
#### CHROMIUM CR

*The Chemical Relations of the Element.*—Chromium gives four classes of compounds, and most of them are colored substances (Gk. *χρῶμα*, color). The **chromates** are derived from chromic acid  $\text{H}_2\text{CrO}_4$ , which, however, is itself unstable, and leaves the anhydride  $\text{CrO}_3$ , when its solution is evaporated. The oxide and hydroxide in which the element is trivalent, namely  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}(\text{OH})_3$ , are weakly basic and still more weakly acidic. Hence we have **chromic salts** such as  $\text{CrCl}_3$  and  $\text{Cr}_2(\text{SO}_4)_3$ , which are somewhat hydrolyzed, but no carbonate, and no sulphide which is stable in water. The compounds in

which the same hydroxide acts as an acid are the **chromites**, and are derived from the less completely hydrated form of the oxide  $\text{CrO}(\text{OH})$ . Potassium chromite  $\text{K}.\text{CrO}_2$  is more easily hydrolyzed, however, than is potassium zincate or potassium aluminate. Finally, the **chromous salts**, such as  $\text{CrCl}_2$  and  $\text{CrSO}_4$ , correspond to chromous hydroxide  $\text{Cr}(\text{OH})_2$ , in which the element is bivalent. This hydroxide is more distinctly basic than is chromic hydroxide, and forms a carbonate and sulphide which can be precipitated in aqueous solution. The chromous salts resemble the stannous and ferrous (*q.v.*) salts in being easily oxidized by the air.

**Occurrence and Isolation.** — Chromium is found chiefly in ferrous chromite  $\text{Fe}(\text{CrO}_2)_2$ , which constitutes the mineral chromite, of which Rhodesia supplied 62,500 long tons and New Caledonia 67,000 in 1915, and in crocoisite  $\text{PbCrO}_4$ , which is chromate of lead. It was first discovered in the latter mineral by Vauquelin (1797). The metal is easily obtained by reduction of the oxide with aluminium filings.

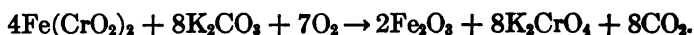
**Physical and Chemical Properties.** — Chromium is a white, crystalline, very hard metal (m.-p.  $1520^\circ$ ). It does not tarnish, but when heated it burns in oxygen, giving the green chromic oxide  $\text{Cr}_2\text{O}_3$ . It seems to exist in two states, an active and a passive one, the relations of which are still somewhat obscure. A fragment which has been made by the Goldschmidt method, or has been dipped in nitric acid, is passive, and does not displace hydrogen from hydrochloric acid. When, however, the specimen is warmed with this acid, it begins to interact, and thereafter behaves as if it lay between zinc and cadmium in the electromotive series. If left in the air, it slowly becomes inactive again. Tin and iron with hydrochloric acid form stannous and ferrous chloride, respectively, because the higher chlorides, if present, would be reduced by the active hydrogen. Here, for the same reason, chromous chloride and not chromic chloride is formed:



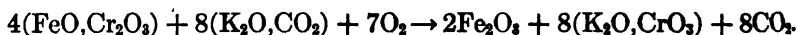
Chromium is used in making chrome-steel, for armorplate. The strange alloys, which, although composed of active metals, are not attacked by acids (even boiling nitric acid) usually contain chromium (*e.g.*, 60 per cent Cr, 36 per cent Fe, 4 per cent Mo).

## DERIVATIVES OF CHROMIC ACID

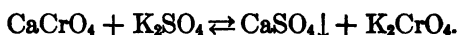
**Potassium Chromate  $K_2CrO_4$ .** — This and the sodium salt, or rather the corresponding dichromates (see below), are made directly from chromite, and form the starting-point in the preparation of the other compounds of chromium. The finely powdered mineral is mixed with potash and limestone, and roasted. The lime is employed chiefly to keep the mass porous and accessible to the oxygen of the air, the potassium compounds being easily fusible:



The iron is oxidized to ferric oxide, and the chromium passes from the state of chromic oxide in the chromite ( $FeO, Cr_2O_3$ ) to that of chromic anhydride in the potassium chromate ( $K_2O, CrO_3$ ). Thus, more insight is given into the nature of the action by the equation:



The cinder is treated with hot potassium sulphate solution. This interacts with the calcium chromate, which is formed at the same time, giving insoluble calcium sulphate:

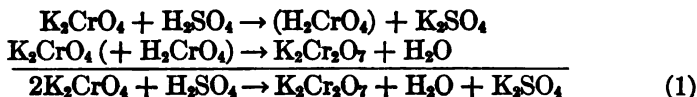


The whole of the potassium chromate goes into solution.

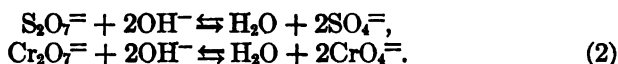
Potassium chromate is pale-yellow in color, rhombic in form (isomorphous with potassium sulphate), and is very soluble in water (61 : 100 at  $10^\circ$ ).

**Sodium chromate  $Na_2CrO_4, 10H_2O$**  is made by using sodium carbonate in the process just described.

**The Dichromates.** — When a solution of potassium sulphate is mixed with an equivalent amount of sulphuric acid, potassium bisulphate is obtainable by evaporation:  $K_2SO_4 + H_2SO_4 \rightarrow 2KHSO_4$ . The dry acid salt, when heated, loses water (p. 437), giving the pyrosulphate (or disulphate):  $2KHSO_4 \rightleftharpoons K_2S_2O_7 + H_2O$ , but the latter, when redissolved, returns to the condition of acid sulphate. Now, when an acid is added to a chromate we should expect the chromic acid  $H_2CrO_4$ , thus liberated, to interact, giving an acid chromate (say,  $KHCrO_4$ ). No acid chromates are known, however, and instead of them, pyrochromates or dichromates are produced, with elimination of water. In other words, the second of the above actions is not appreciably reversible when chromates are in question:



In terms of ions,  $\text{S}_2\text{O}_7^{=}$  is unstable in water, and interacts with the  $\text{OH}^-$  ion it contains, giving water and sulphate-ion, while  $\text{Cr}_2\text{O}_7^{=}$  is stable in water and is formed from the interaction of water and chromate-ion:



The dichromates of potassium and sodium are made by adding sulphuric acid to the crude solution of the chromate obtained from chromite (p. 856). They crystallize when the liquid cools, and the mother-liquor, containing the potassium sulphate and undeposited dichromate, is used for extracting a fresh portion of cinder. As the dichromates are much less soluble than the chromates, they crystallize from less concentrated solutions, and can therefore be obtained in purer condition. Hence the extract is always treated for dichromate.

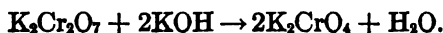
**Potassium dichromate**  $\text{K}_2\text{Cr}_2\text{O}_7$  (or  $\text{K}_2\text{CrO}_4, \text{CrO}_3$ ) crystallizes in asymmetric tables of orange-red color. Its solubility in water is 8:100 at  $10^\circ$  and 12.5:100 at  $20^\circ$ . **Sodium dichromate**  $\text{Na}_2\text{Cr}_2\text{O}_7, 2\text{H}_2\text{O}$  forms red crystals also, and its solubility is 109:100 at  $15^\circ$ . This salt is now cheaper than potassium dichromate, and has largely displaced the latter for commercial purposes.

By treatment of the chromates with larger amounts of free acid, other polychromates are formed. Thus, with increasing amounts of nitric acid, ammonium chromate gives first the dichromate  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ , which may be written  $(\text{NH}_4)_2\text{CrO}_4, \text{CrO}_3$ , then the trichromate  $(\text{NH}_4)_2\text{CrO}_4, 2\text{CrO}_3$ , and even the tetrachromate  $(\text{NH}_4)_2\text{CrO}_4, 3\text{CrO}_3$ , all of which are red crystalline substances.

**Chemical Properties of the Dichromates.**—1. When concentrated sulphuric acid is added to a strong solution of a dichromate (or chromate), **chromic anhydride**  $\text{CrO}_3$  separates in red needles:

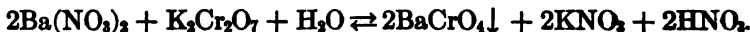


2. Although a dichromate lacks the hydrogen, it is essentially of the nature of an acid salt, just as  $\text{SbOCl}$  lacks hydroxyl, but is essentially a basic salt. Hence, when potassium hydroxide is added to a solution of potassium dichromate, potassium chromate is formed:



The solution changes from red to yellow, and the chromate is obtained by evaporation. In this way the pure alkali chromates are made.

3. By addition of potassium dichromate to a solution of a salt of a metal whose chromate is insoluble, the chromate, *not* the dichromate, is precipitated. This occurs because there is always a little  $\text{CrO}_4^{=}$  (equation (2), above) in the solution of the dichromate:



Being essentially an acid salt, the dichromate produces a salt and an acid, as any acid salt would do. For example:

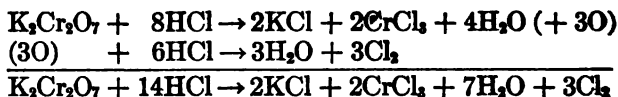


Soluble chromates, naturally, also precipitate insoluble ones.

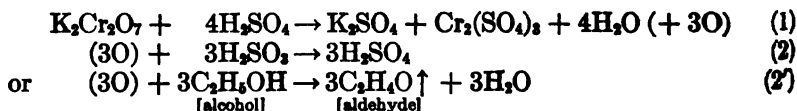
4. The dichromates of potassium and sodium melt when heated, and, at a white heat, decompose, giving the chromate, chromic oxide, and free oxygen. To make the equation, we note that the dichromate, for example  $\text{K}_2\text{Cr}_2\text{O}_7$ , consists of  $\text{K}_2\text{CrO}_4 + \text{CrO}_3$ , and the latter, if alone, will decompose thus:  $2\text{CrO}_3 \rightarrow \text{Cr}_2\text{O}_3 + 3\text{O}$ . Since the product must contain a multiple of  $\text{O}_2$ , the equation is:



5. With free acids, the dichromates give powerful oxidising mixtures, in consequence of their tendency to form chromic salts. Since the former correspond to the oxide  $\text{CrO}_3$  and the latter to  $\text{Cr}_2\text{O}_3$ , the passage from the former to the latter must furnish  $3\text{O}$  for every  $2\text{CrO}_3$  transformed. In dilute solutions, unless a body capable of being oxidized is present, no actual decomposition, beyond the liberation of dichromic acid\* occurs. When concentrated hydrochloric acid is used, this acid itself suffers oxidation:



When sulphuric acid is employed, an oxidizable substance such as hydrogen sulphide (*cf.* p. 418), sulphurous acid, or alcohol must be present, if the dichromate is to be reduced:



\* Not shown as a distinct stage in the subsequent equations.

In each case the usual summation of (1) and (2), with omission of the 3O gives the equation for the whole action. When (1) is dissected,  $K_2O, 2CrO_3$  giving  $Cr_2O_3, 3SO_3 + 3O$  is found to be its essential content. In practice, this sort of action is used for the purpose of making chromic salts, and for its oxidizing effects, as in the preparation of aldehyde and in the dichromate battery (p. 797).

6. When a body which is not merely oxidizable, but is an active reducing agent, is employed, the dichromate may be reduced without the addition of any acid. For example, when warmed with ammonium sulphide, a dichromate gives chromic hydroxide and free sulphur:



**Applications of Dichromates.** — If the reducing body is less active, the change may nevertheless take place under the influence of light. Thus, when paper is coated with gelatine containing a soluble chromate or dichromate, and, after being dried, is exposed to light, chromic oxide is formed by reduction, and is adsorbed by the gelatine, which is a colloid. This product will not swell up or dissolve in tepid water, as does pure gelatine. This action is used in many ways for purposes of artistic reproduction. Thus, if the gelatine mixture is made up with lampblack, and, after the coating has dried, is covered with a negative and exposed to light, the parts which were protected from illumination may afterwards be washed away, while the **carbon print** remains. The gelatine layer can be transferred to wood or copper before washing. When materials of different colors are substituted for the lampblack, prints of any desired tint may be made by the same process.

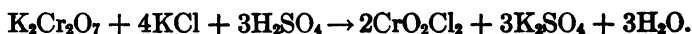
Sodium dichromate is used, instead of tan-bark, in tanning kid and glove leathers (**chrome-tanning process**). A reducing agent is employed to precipitate chromic hydroxide  $Cr(OH)_3$  in the leather. Its use diminishes the time required for tanning from 8 or 10 months to a few hours. The hide is a mixture of colloidal materials, and the chromic hydroxide is adsorbed.

**Insoluble Chromates.** — A number of chromates, formed by precipitation with a solution of a soluble chromate or dichromate, are familiar. Thus, **lead chromate**  $PbCrO_4$  is used as a yellow pigment. By treatment with limewater it gives a basic salt of brilliant orange color — **chrome-red**  $Pb_2OCrO_4$ . Salts of calcium give a yellow, hy-

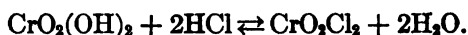


drated **calcium chromate**  $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$  analogous to gypsum and, like it, perceptibly soluble in water (0.4 : 100 at  $14^\circ$ ). **Barium chromate**  $\text{BaCrO}_4$  is also yellow. It interacts with active acids to form the dichromate, and passes into solution. Like calcium oxalate (*cf.* p. 714), it is not soluble enough to be attacked by acetic acid. **Strontium chromate**  $\text{SrCrO}_4$ , however, interacts with acetic acid. **Silver chromate**  $\text{Ag}_2\text{CrO}_4$  is red, and interacts easily with acids. It will be observed that there is a close correspondence between the relative solubilities (see Table) of the chromates and the sulphates.

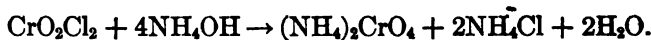
**Chromyl Chloride**  $\text{CrO}_2\text{Cl}_2$ . — This compound corresponds to sulphuryl chloride  $\text{SO}_2\text{Cl}_2$ , and is made by distilling a dichromate with a chloride and concentrated sulphuric acid:



The hydrochloric acid liberated from the chloride may be supposed to interact with chromic acid from the dichromate:



Chromyl chloride is a red liquid (b.-p.  $118^\circ$ ). It fumes strongly in moist air, being hydrolyzed by water (read the last equation backwards). The corresponding bromine and iodine compounds are unstable, and when a bromide or iodide is treated as described above, the halogens are liberated by oxidation, and no volatile compound of chromium appears. Hence, when an unknown halide is mixed with potassium dichromate and sulphuric acid and distilled, and the vapors are caught in ammonium hydroxide, the finding of a chromate in the distillate demonstrates the existence of a chloride in the original mixture:



This action is used as a test for the presence of traces of chlorides in large amounts of bromides or iodides, or both.

**Chromic Anhydride**  $\text{CrO}_3$ . — This oxide is made as described above (par. 4, p. 857), and is often called "chromic acid." It is soluble in water, and combines with the latter to some extent, giving dichromic acid  $\text{H}_2\text{Cr}_2\text{O}_7$ . In a solution acidified with an active acid it is much used as an oxidizing agent for organic substances. It interacts with acids in the same way as do the dichromates, giving chromic salts and furnishing oxygen to the oxidizable body. When

heated by itself, it loses oxygen readily, leaving the green chromic oxide:  $4\text{CrO}_3 \rightarrow 2\text{Cr}_2\text{O}_3 + 3\text{O}_2$ .

#### CHROMIC AND CHROMOUS COMPOUNDS

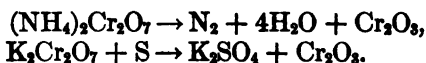
**Chromic Chloride.**—A hydrated chloride  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  is obtained by treating the hydroxide  $\text{Cr}(\text{OH})_3$  with hydrochloric acid and evaporating. When heated, it is hydrolyzed, and chromic oxide remains. The anhydrous chloride  $\text{CrCl}_3$  is formed by sublimation, as a mass of brilliant, reddish-violet scales, when chlorine is led over heated metallic chromium.

In this form the substance dissolves with extreme slowness, even in boiling water, but in presence of a trace of chromous chloride, or stannous chloride it is easily soluble. The solution is green, as are all solutions of chromic salts after they have been boiled, but on standing in the cold, bluish crystals of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  are deposited. These give a violet solution containing  $\text{Cr}^{+++} + 3\text{Cl}^-$ , but boiling reproduces the green color. The green material can also be obtained in crystals as a hexahydrate, and is therefore isomeric (p. 583) with the violet variety. With the green isomer, in cold solution, silver nitrate precipitates at first only one-third of the chlorine as silver chloride.

**Chromic Hydroxide.**—When ammonium hydroxide is added to a solution of a chromic salt, a hydrated hydroxide of pale-blue color,  $2\text{Cr}(\text{OH})_3 \cdot \text{H}_2\text{O}$ , is thrown down. This loses water by stages, giving intermediate hydroxides such as  $\text{Cr}(\text{OH})_3$  and  $\text{CrOOH}$ , and finally  $\text{Cr}_2\text{O}_3$ . It interacts with acids, giving chromic salts. It also dissolves in potassium and sodium hydroxides to form green solutions of **chromites** of the form  $\text{KCrO}_2$ . When the solutions of the alkali chromites are boiled, the free hydroxide, present in consequence of hydrolysis, is converted into a greenish, less completely hydrated, and less soluble variety. This begins to come out as a precipitate, and soon the whole action is reversed. Insoluble chromites, such as that of iron  $\text{Fe}(\text{CrO}_2)_2$ , are found in nature. Many of them, like  $\text{Zn}(\text{CrO}_2)_2$  and  $\text{Mg}(\text{CrO}_2)_2$ , may be formed by fusing the oxide of the metal with chromic oxide; the action being similar to that used in making zincates (p. 771) and aluminates (p. 812). The hydroxide is used as a mordant (p. 820) and is the active substance in the chrome-tanning process (p. 859).

**Chromic Oxide  $\text{Cr}_2\text{O}_3$ .**—This oxide is obtained as a green, infusible powder by heating the hydroxide, or, more readily, by heat-

ing dry ammonium dichromate; or by igniting potassium dichromate with sulphur and washing the potassium sulphate out of the residue:



Chromic oxide is not affected by acids, but may be converted into the sulphate by fusion with potassium bisulphate. It is **used** for making green paint, and for giving a green tint to glass. When the oxide, or any of the chromic salts, is fused with a basic substance such as an alkali carbonate, it passes into the form of a chromate, absorbing the necessary oxygen from the air. If an alkali nitrate or chlorate is added, the oxidation goes on more quickly. The alkaline solution of the chromites may be oxidized, for example, by addition of chlorine or bromine, and chromates are formed.

**Chromic Sulphate**  $\text{Cr}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$ . — This salt crystallizes in reddish-violet crystals, and may be made by treating the hydroxide with sulphuric acid. When mixed with potassium sulphate solution, it gives reddish-violet, octahedral crystals of **chrome-alum** (*cf.* p. 813),  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . This double salt is most easily obtained by reducing potassium dichromate in dilute sulphuric acid by means of sulphurous acid (p. 858), and allowing the solution to crystallize. The solution of the crystals, either of the pure sulphate or of the alum, is bluish-violet ( $\text{Cr}^{+++}$ ), but when boiled becomes green. The green compound is formed by hydrolysis and is gummy and uncrystallizable. It even yields products which do not show the presence either of the  $\text{Cr}^{+++}$  or the  $\text{SO}_4^{=}$  ion. It seems to be formed thus:



The green materials revert slowly to the violet ones by reversal of the above action when the solution remains in the cold, and so crystals of the sulphate or of the alum are obtainable from the green solutions.

**Chromic Acetate**. — This salt,  $\text{Cr}(\text{CO}_2\text{CH}_3)_3$ , is made by treating the hydroxide with acetic acid, and a green solution of it is used as a mordant by calico-printers (*cf.* p. 820).

**Chromous Compounds**. — By the interaction of chromium with hydrochloric acid, or by reducing chromic chloride in a stream of hydrogen, **chromous chloride**  $\text{CrCl}_2$  is formed. The anhydrous salt is colorless, and its solution is blue ( $\text{Cr}^{++}$ ). Like stannous chloride,

it is very easily oxidized by the air, a solution of it containing excess of hydrochloric acid being used in the laboratory to absorb oxygen:



**Chromous hydroxide**  $\text{Cr}(\text{OH})_2$  is obtained as a yellow precipitate when alkalis are added to the chloride. With sulphuric acid it gives **chromous sulphate**  $\text{CrSO}_4 \cdot 7\text{H}_2\text{O}$ , which is one of the vitriols (p. 771).

Chromous salts give with ammonium sulphide a black precipitate of **chromous sulphide**  $\text{CrS}$ , and with sodium acetate a red precipitate of **chromous acetate**. The latter is not very soluble, and is less quickly oxidized by the air than any of the other chromous compounds.

**Analytical Reactions of Chromium Compounds.**—The chromic salts give the bluish-violet chromic-ion  $\text{Cr}^{+++}$ , or the green complex cations, and may be recognized in solution by their color. The chromates and dichromates give the ions  $\text{CrO}_4^{=}$  and  $\text{Cr}_2\text{O}_7^{=}$ , which are yellow and red, respectively. From chromic salts, alkalis and ammonium sulphide precipitate the bluish-green hydroxide, and carbonates give a basic carbonate which is almost completely hydrolyzed to hydroxide. By fusion with sodium carbonate and sodium nitrate, they yield a yellow bead containing the chromate. The chromates and dichromates are recognized by the insoluble chromates which they precipitate, and by their oxidizing power when mixed with acids. All compounds of chromium give a green borax bead containing chromic borate, and this bead differs from that given by compounds of copper (*cf.* p. 746), which is also green, in being unreducible.

#### MOLYBDENUM, TUNGSTEN, URANIUM

As was stated at the opening of the chapter, these elements give acid anhydrides of the form  $\text{XO}_3$ , and acids and salts of the form  $\text{H}_2\text{XO}_4$ . They also give salts of the form  $\text{H}_2\text{X}_2\text{O}_7$  corresponding to the dichromates. Uranium has base-forming properties as well.

**Molybdenum.**—This element is found chiefly in wulfenite  $\text{PbMoO}_4$  and molybdenite  $\text{MoS}_2$ . The latter resembles black lead (graphite), and its appearance suggested the name of the element (Gk. *μόλυβδαινα*, lead). The molybdenite is converted by roasting into **molybdic anhydride**  $\text{MoO}_3$ . When this is treated with ammonium hydroxide, or with sodium hydroxide, **ammonium molybdate**  $(\text{NH}_4)_2\text{MoO}_4$ , or **sodium molybdate**  $\text{Na}_2\text{MoO}_4 \cdot 10\text{H}_2\text{O}$  is obtained.

The **metal** itself is liberated by reducing the oxide or chloride with hydrogen. When pure it is a silvery metal and, like iron (*q.v.*), takes up carbon and shows the phenomena of tempering. The **oxides**  $\text{Mo}_2\text{O}_3$ ,  $\text{MoO}_2$ , and  $\text{MoO}_3$  are known, but the lower oxides are not basic. The **chlorides**  $\text{Mo}_3\text{Cl}_8$ ,  $\text{MoCl}_3$ ,  $\text{MoCl}_4$ , and  $\text{MoCl}_5$  have been made. The chief use of molybdenum compounds in the laboratory is in **testing for and estimating phosphoric acid**. When a little of a phosphate is added to a solution of ammonium molybdate in nitric acid, and the mixture is warmed, a copious yellow precipitate of a **phosphomolybdate of ammonium**  $(\text{NH}_4)_3\text{PO}_4 \cdot 11\text{MoO}_3 \cdot 6\text{H}_2\text{O}$  is formed. The compound is soluble in excess of phosphoric acid and in alkalis, but not in dilute mineral acids.

**Tungsten.**—The minerals scheelite  $\text{CaWO}_4$  and wolfram  $[\text{Fe}, \text{Mn}]\text{WO}_4$  are tungstates of calcium and of iron and manganese, respectively. By fusion of wolfram with sodium carbonate and extraction with water, **sodium tungstate**  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  is secured. It is used as a mordant and for rendering muslin fireproof. Acids precipitate **tungstic acid**  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$  from solutions of this salt. The element gives the **oxides**  $\text{WO}_2$  and  $\text{WO}_3$ , the latter being formed by ignition of tungstic acid. The **chlorides**  $\text{WCl}_2$ ,  $\text{WCl}_4$ ,  $\text{WCl}_5$ , and  $\text{WCl}_6$  are known, the last being formed directly, and the others by reduction.

The metal has important **uses**, and the annual production is greater than the total of all the metals which follow it in the list on p. 645. The metal (density 19.6) can be liberated by reduction of the oxide by hydrogen or by carbon. It has a higher melting-point ( $3540^\circ$ ) than has any other metal, and, on this account, and because it is less volatile than carbon, is now used for filaments in electric lamps. A carbon filament also requires 3.25 watts per candle power while a tungsten filament uses only 1.25 watts per 1 c.-p. and lasts twice as long. The powdered metal obtained by reduction can be pressed into wire form and then rolled while strongly heated by an electric current until a compact wire is obtained. The metal can also be obtained in massive form by reducing the oxide with aluminium, provided the crucible and mixture are heated strongly in advance. In 1914, in the United States alone, about a hundred million tungsten lamps were manufactured. Shop work has been almost revolutionized by the use of **tungsten steel tools**, which can be used at high speed and, even when thus heated red hot by friction, retain their temper. Tungsten steel contains tungsten (16 to 20 per cent),

carbon (0.55 to 0.75 per cent), chromium (2.5 to 5 per cent), and vanadium (0.35 to 1.5 per cent).

**Uranium.** — Pitchblende, which contains the oxide  $U_3O_8$  along with smaller amounts of many other elements, is found mainly in Joachimsthal (Bohemia) and in Cornwall. Carnotite, a uranate and vanadate of potassium  $K_2O, 2UO_3, V_2O_5, 3H_2O$ , occurs in Colorado. Pitchblende is roasted with lime, the calcium uranate  $CaUO_4$  thus formed is decomposed with sulphuric acid, giving **uranyl sulphate**  $UO_2SO_4$ . When excess of sodium carbonate is added to the solution of the latter, the foreign metals are precipitated and **sodium diuranate**  $Na_2U_2O_7, 7H_2O$ , which is also thrown down, dissolves in the excess as  $Na_2UO_4$ .

After filtration, the diuranate of sodium is reprecipitated by neutralizing with sulphuric acid and boiling. This salt is used in making **uranium glass**, which shows a yellowish-green fluorescence. The property is due to the fact that the wave-length of part of the invisible, ultra-violet rays of the sunlight are lengthened, and a greenish light is therefore in excess. The **oxides** are  $UO_2$ , a basic oxide,  $U_2O_3$ ,  $U_3O_8$  the most stable oxide,  $UO_3$  uranic anhydride, and  $UO_4$  a peroxide.

When the oxide  $UO_2$  is treated with acids, it gives uranous salts such as **uranous sulphate**  $U(SO_4)_2, 4H_2O$ . Uranic anhydride and uranic acid interact with acids, giving basic salts, such as  $UO_2SO_4, 3\frac{1}{2}H_2O$ , and  $UO_2(NO_3)_2, 6H_2O$ , which are named **uranyl sulphate**, **uranyl nitrate**, and so forth. They are yellow in color, with green fluorescence. Ammonium sulphide throws down the brown, unstable **uranyl sulphide**  $UO_2S$  from their solutions.

#### RADIOACTIVE ELEMENTS

**Historical.** — We have seen (p. 469) that in an evacuated tube, through which an electric discharge is passed, the "rays" emanating from the cathode (**cathode rays**) strike the anti-cathode and the glass beyond it. Cathode rays were discovered by Sir William Crooks (1878), and later were shown to consist of particles of negative electricity or **electrons**, each having a mass about  $\frac{1}{1837}$  of that of an atom of hydrogen. They produce in the glass a greenish-yellow, fluorescent light. Röntgen (1895) accidentally discovered that this light (**X-rays**) penetrated paper, flesh, and other materials composed of elements of low atomic weight and acted upon photo-

graphic plates. In 1896 Henri Becquerel observed that minerals containing uranium gave off a sort of radiation which could penetrate black paper, that was opaque to ordinary light, and reduce the silver bromide on a photographic plate placed beneath the papers. He also discovered that an electrometer (Fig. 161), in which the gold leaves

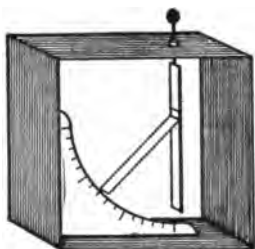


FIG. 161.

had been caused to separate by charging with electricity, lost its charge rapidly when the uranium ore (or salt) was brought near (3-4 cm.) to the knob connected with the leaves. The uranium material rendered the air a conductor ("ionized" the air) and this effect permitted the escape of the electric charge, which otherwise would have been retained for a considerable time. In

the quantitative measurement of radioactivity, we now compare the times required for the discharge of an electrometer by different specimens of radioactive matter. The presence of  $10^{-12}$  g. of such matter can thus be detected.

The radioactivity of every pure uranium compound is proportional to its uranium content. The *ores* are, however, relatively four times as active. This fact led M. and Mme. Curie, just after 1896, to the discovery that the pitchblende residues, from which practically all of the uranium had been extracted, were nevertheless quite active. About a ton of the very complex residues having been separated laboriously into the components, it was found that a large part of the radioactivity remained with the sulphate of barium. From this barium sulphate, a product free from barium, and at least one million times more active than uranium, was finally secured in the form of the bromide. The nature of the spectrum and the chemical relations of the element, now named **radium**, placed it with the metals of the alkaline earths. The ratio by weight of chlorine to radium in the chloride is 35.46 : 113, so that, on the assumption that the element is bivalent, its chloride is  $\text{RaCl}_2$  and its atomic weight is 226. With this value it occupies a place formerly vacant in the periodic table.

In 1910 Mme. Curie obtained metallic radium by electrolyzing a solution of radium chloride, using a mercury cathode, and expelling the mercury by distillation. It was a white metal (m.-p.  $700^\circ$ ) which, like calcium, quickly tarnished in the air and displaced hydrogen from water.

**The Nature of the "Rays."** — Many properties show that the "rays" emitted by compounds of uranium and of radium are of three kinds. They are most sharply distinguished from one another when allowed to pass through a powerful magnetic field. The **alpha-rays** are positively charged and are bent in one direction while the **beta-rays** are negative and are bent in the other. The **gamma-rays** are not affected.

The **alpha-rays** are atoms of **helium** (p. 511) thrown off in straight lines with varying initial velocities, averaging about one-tenth that of light (say, 30,000 kilometers per second. The  $\alpha$ -particles from Ra-C, *e.g.*, 19,220 kilom. per sec.). Each such atom bears a double positive charge (the unit being the charge on a univalent positive ion), and a delicate electroscope readily indicates the entrance of a single atom. These alpha-particles, being each four times as heavy as an atom of hydrogen, plough their way *through* tens of thousands of air-molecules and usually go about 3-8 cm. before being stopped. The emission of atoms of helium can be detected by means of Crookes **spinthariscopes** (Fig. 162). The particle of radium bromide is at *B*, and some of the charged helium atoms strike a surface *C* covered with zinc sulphide, producing faint flashes of light. The lens *A* magnifies the flashes and the latter can be seen in a dark room after the eye has become thoroughly rested (15-20 minutes). The helium gas given off by radium compounds was collected by Soddy, working in Ramsay's laboratory and identified, and its rate of production was measured. The amount was equal to 158 cubic mm. per 1 g. of radium per year.

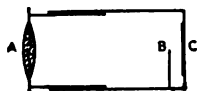


Fig. 162.

The alpha-particles, in passing through the air-molecules, ionize the air, and the ionized air has the same power that dust possesses (p. 505) of affording nuclei on which moisture can condense. Hence, when a particle of a radium compound is supported in a flask containing air saturated with moisture, and the air is suddenly cooled by expansion, the paths of the particles become lines of fog. With powerful illumination, the fog-tracks (Fig. 163) can be photographed (C. T. R. Wilson), and the lengths of the paths can be measured.

The **beta-particles** are **electrons** (p. 354), or unit charges of negative electricity, and are shot out with a velocity approaching that of light (300,000 kiloms. per sec.). They are therefore identical with cathode rays, but move many times more rapidly. Being very light (weight,  $\frac{1}{1836}$  of an atom of hydrogen), their paths, although



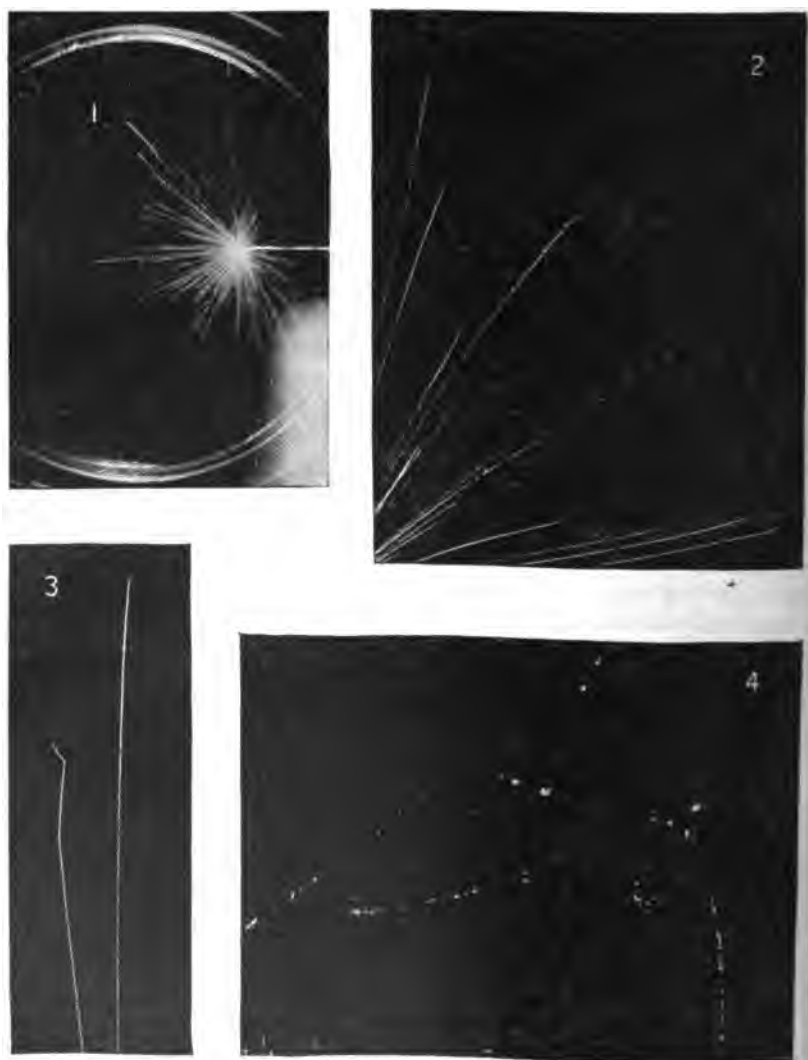


FIG. 163.

straight at first, soon become tortuous owing to collisions with the relatively massive air-molecules. Half of them are lost after going about 4 cm. Their fog tracks are fainter than are those of the  $\alpha$ -particles and extremely tangled. Being much lighter than  $\alpha$ -particles, their paths are actually coiled into circles or spirals by a magnetic field.

The **gamma-rays** are identical with X-rays (vibrations in the ether of short wave-length, p. 469), and are produced, like the latter, by the impacts of the electrons on the surrounding matter.

The helium atoms are almost all stopped by a sheet of paper or by aluminium foil 0.1 mm. thick. The electrons have greater penetrating power, many passing through gold-leaf, but being practically all stopped by a sheet of aluminium 1 cm. thick. The gamma-rays (X-rays), however, are able to penetrate relatively thick layers of metals and other materials of low atomic weight.

One of the most striking facts is that the stoppage by the air of so many rapidly moving particles results in the production of much heat. One gram of radium would produce about 120 cal. per hour.

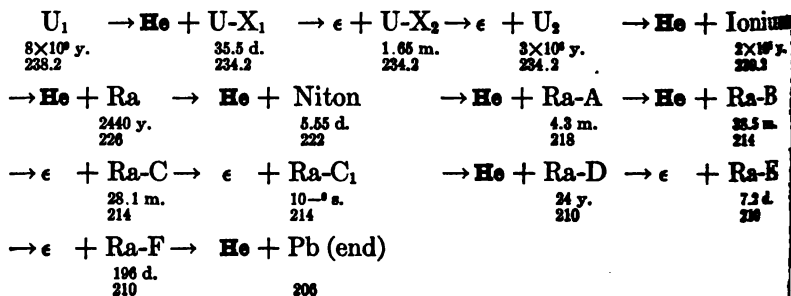
**Disintegration.** — The emission of atoms of helium and of electrons was first explained by Rutherford (1902-3), then of McGill University, Montreal, as being due to the spontaneous disintegration of the atoms of uranium, radium, and other radioactive elements. Thus, Rutherford was the first to show that radium compounds produced a gaseous substance called the radium emanation (niton), which was the residue left after the emission of one atom of helium from an atom of radium. This gas was itself radioactive and underwent further disintegration, depositing a solid radioactive residue on bodies in contact with it. Furthermore, every known uranium ore contains radium (McCoy) and radium emanation (Boltwood) in amounts proportional to the uranium content. Also, after the radium has been removed, the pure uranium compound gives off at first only  $\alpha$ -particles, but gradually recovers its whole radioactivity and is then found to contain radium emanation once more (Soddy). It thus appears that uranium is the starting point, and that the disintegration proceeds by steps, producing a number of different products. Each of these is formed from one such product and by disintegration furnishes another.

Unlike ordinary chemical change, the rate of disintegration is not affected by conditions. It can neither be started nor stopped at will. It is no more vigorous at 2000° than at -200°. Other changes occur *between* atoms, these *within* each atom.

The law, due also to Rutherford, describing the rate at which any one radioactive element disintegrates is simple. Only a certain fraction of the whole of any one specimen undergoes the change in unit time. Thus, as the total amount diminishes because of the change, the amount changing during the next unit of time, being a constant fraction of the whole, must be less. Hence an infinite time would be required for the complete disintegration of any one specimen. For convenience, therefore, it is sometimes the custom to give as a specific property of each radioactive element the time required for the decay of half its amount and therefore the loss of half of its radioactivity. More usually, the property given is the one called the **average life of the element**. The value of this is equal to the inverse of the fraction disintegrating per unit time, and is about 1.44 times the period of half change. Numerically it is the sum of the separate periods of future existence of all the atoms divided by the number of such atoms present at the starting point.

Radium emits helium atoms at the rate of  $3.4 \times 10^{10}$  per gram per second. From this fact, we can calculate its average life to be about 2400 years. Hence, if it were not continuously being produced (from uranium), the whole supply would have been exhausted long before the earth reached a habitable condition.

**The Uranium Group of Radioactive Elements.**—The following shows the various elements produced from uranium by successive disintegrations. When a helium atom or an electron is expelled, the fact is shown by the symbols He and  $\epsilon$ , respectively. The first number below each element is the average life of that member of the series (y. = year, d. = day, h. = hour, m. = minute, s. = second). The second number is the atomic weight, obtained by subtracting from the at. wt. of uranium (238.2) the weight (4) of each helium atom emitted.



A purified salt of uranium recovers half its activity in about three weeks, and reaches full equilibrium in from six months to a year. An equilibrium is attained when the speed at which each disintegration product is being formed is balanced by the equal speed with which it is passing into the next member of the series. The complex operations required for studying all the members of the series cannot be given here. It may be said, however, that a pure uranium salt in solution gives with ammonium carbonate a precipitate which is wholly soluble in excess of the reagent. After about a year, another portion of the same specimen leaves a slight precipitate which is insoluble in excess and contains the products of disintegration, chiefly U-X, which was first obtained in this way by Crookes.

The radium emanation was shown by Ramsay to be one of the inert gases (p. 511), and was renamed *niton*. Its density was determined experimentally with a small sample, using a micro-balance capable of weighing to 1/500,000 mgm., and found to be about 222.4 (density of oxygen = 32).

The end-product of the disintegration is lead, and all uranium ores contain lead. Lead from other sources gives a chloride  $\text{PbCl}_2$  in which 207.20 parts of lead are combined with  $2 \times 35.46$  parts of chlorine. The atomic weight 207.2 cannot, however, be reached by subtracting a whole number of atomic weights of helium from the atomic weight of uranium, the number 206 being obtained instead. Recently, lead chloride prepared from the lead found in various ores of uranium has been analyzed by Richards of Harvard, as well as, independently, by two other chemists, and the atomic weight of this lead was found to be from 206.05 to 206.8 in different samples. This lead chloride has properties *identical* with those of ordinary lead chloride and is, therefore, by definition, the same substance. Hence these investigations have revealed the first known exception to the law of definite proportions. Metallic lead from radium ores has the density 11.288 (Richards, 1916), however, that of ordinary lead being 11.337 (19.94°), which gives the same atomic volume for both. The spectra of these leads are identical.

Since the initial (U) and final (Pb) materials are both electrically neutral, it must be assumed that at some stages more than one electron per atom is expelled.  $8\text{He}^{++}$  are lost and therefore  $16e^-$ .

**Additional Data.**—The yield of radium is very small. 6000 kg. of pitchblende, after extraction of the uranium, yield about

2000 kg. of residue. This affords about 6 to 8 kg. of the mixture of radium and barium sulphates, from which 0.2 g. of pure radium bromide can be prepared.

One gram of uranium, after it has produced the equilibrium proportion of radium (about  $3.2 \times 10^{-7}$  g.), gives off helium at the rate of 1 c.c. in sixteen million years. Since the mineral fergusonite contains 26 c.c. of accumulated helium for every gram of uranium, the samples of this mineral must be at least 416 million years old.

The complete disintegration of 1 c.c. of niton to lead would deliver about seven million calories, but, of course, the liberation of the heat would be spread over a great length of time.

**Chemical Actions of the "Rays."** — The radiations which are most active in ionizing air and in acting upon photographic plates are the  $\alpha$ -particles. These particles also cause the flashes of light when they encounter zinc sulphide. The radiations change the colors of minerals, including gems, and give a deep violet color to the glass tube containing the specimen. They also turn atmospheric oxygen in part into ozone and, in solution, produce traces of hydrogen peroxide in the water.

The radiations also destroy minute organisms and kill the cells of the skin, producing sores. They have been employed in the treatment of lupus and of superficial cancerous growths.

**Other Radioactive Series.** — Thorium, found as phosphate in monazite sand, is also radioactive and furnishes a series of disintegration products. The final material is a salt of lead. Analysis of the chloride of lead made from traces of the element found in all thorium minerals shows that the atomic weight (Soddy) is 208.4, while that of ordinary lead is 207.2. The atom of thorium (at. wt. 232.4) thus loses  $6\text{He}$  ( $= 6 \times 4 = 24$ ) during the disintegration. There are thus three chlorides of lead with identical properties, but different compositions, namely, the common one  $207.2 : 2 \times 35.46$ , that from radium  $206 : 2 \times 35.46$ , and that from thorium  $208.4 : 2 \times 35.46$ .

Actinium and polonium are also radioactive elements, which have not yet been fully investigated. The former appears to be formed by a second, parallel, disintegration of  $\text{U}_1$ , and the latter in a similar way from  $\text{Ra-E}$ . Compounds of potassium and rubidium show traces of radioactivity.

**Significance of Radioactivity.**—The Brownian movement (p. 622) has revealed to us bodies intermediate between ordinary particles and single molecules, and has enabled us to estimate the actual weight of molecules. Radioactivity enables us to count charged molecules of helium as they enter the electroscope or produce flashes of light on zinc sulphide, and the fog-tracks permit us to follow their movements. There is thus now no question that molecules and atoms are real. Furthermore, we infer that all kinds of atoms are composed of a positive nucleus (p. 470) surrounded by electrons, although only the atoms of radioactive elements are unstable. The diameter of the positive nucleus of a hydrogen atom is calculated to be about  $\frac{1}{1800}$  of that of an electron. Rutherford has confirmed this by actual measurement. The atom is thus no longer regarded as being solid and continuous in structure. It is mainly a vacuum, containing a few relatively very minute bodies possessing weight. The fact that  $\alpha$ -particles are thus able to plough their way through molecules of oxygen and nitrogen, being diverted from a straight path only when they happen to pass very close to the positive nucleus (which, of course, repels the positive  $\alpha$ -particles), is no longer mysterious.

Another interesting conclusion has been reached from the observation that niton is found in the soil and in many natural waters. Calculation shows that the heat given off by the disintegration of the amounts of radioactive matter known to exist in the crust of the earth is alone sufficient to account for the maintenance of the temperature of the planet. A globe of the size and material of the earth, possessing originally only heat energy, and cooling from a white hot condition to the temperature of interstellar space, would have passed through the stage of habitable temperatures in a much shorter time than that which a study of the geological deposits (and the fossils they contain) show to have been actually available. The discovery of the enormous, but gradually released disintegration energy of the radioactive elements enables us now to explain the prolonged period during which life has existed on the earth.

**Exercises.**—1. Construct equations, showing the interactions of: (a) chromic oxide and aluminium, (b) strontium nitrate and potassium dichromate in solution, (c) potassium hydroxide and chromic hydroxide, and the reversal on boiling, (d) chlorine and potassium chromite in excess of alkali (what is the actual oxidizing agent?).

2. What volume of oxygen at  $0^{\circ}$  and 760 mm., (a) is obtainable from one formula-weight of potassium dichromate (par. 4, p. 858), (b) is required to oxidize one formula-weight of chromous chloride?

3. To what classes of actions should you assign the three methods of making chromic oxide (p. 861)?

4. Make equations for all the reactions involved in the preparation of sodium-diuranate from pitchblende.

5. How many candle power will be obtained from 50-watt carbon and tungsten filament lamps, respectively?

6. Point out the resemblance, and the differences between the reactions of, (a) gold with *aqua regia*, (b) calcium oxalate with hydrochloric acid, (c) barium chromate with nitric acid (p. 860).

## CHAPTER XLIII

### MANGANESE

**The Chemical Relations of the Element.** — Manganese stands, at present, alone on the left side of the eighth column of the periodic table. The right side is occupied by the halogens. It is never univalent, as are the halogens, but its heptoxide  $Mn_2O_7$  and the corresponding acid, permanganic acid  $HMnO_4$ , are in many ways closely related to the heptoxide of chlorine and perchloric acid  $HClO_4$ . Of the lower oxides of manganese,  $MnO$  is basic, and  $Mn_2O_3$  feebly basic.  $MnO_2$  is feebly acidic,  $MnO_3$  more strongly so, and permanganic acid (from  $Mn_2O_7$ ) is a very active acid. Contrary to the habit of feebly acidic and feebly basic oxides, such as those of zinc, aluminium, and tin, the basic oxides of manganese are not at all acidic, and the acidic oxides, with the exception of  $MnO_3$ , are not also basic. There are thus the five following, rather well-defined sets of compounds, showing five different valences of the element. Of these the first, fourth, and fifth are the most stable and the most important.

• 1. **Manganous compounds**,  $MnO$ ,  $Mn(OH)_2$ ,  $MnSO_4$ , etc. These compounds resemble those of the magnesium family (and those of  $Fe^{++}$ ). The salts of weak acids, such as the carbonate and sulphide, are easily made, and there is little hydrolysis of the halides. The salts are pale-pink in color.

2. **Manganic compounds**,  $Mn_2O_3$ ,  $Mn(OH)_3$ ,  $Mn_2(SO_4)_3$ ,  $[MnCl_3]$ . The salts resemble the chromic and aluminium salts in behavior, but are even less stable than are those of quadrivalent lead. They are completely hydrolyzed by little water. The salts are violet in color.

3. **Manganites**,  $MnO_2$ ,  $H_2MnO_3$ ,  $CaMnO_3$ . The alkali manganites are strongly hydrolyzed, like the plumbates and the stannates.

• 4. **Manganates**,  $MnO_3$ ,  $H_2MnO_4$ ,  $K_2MnO_4$ . The salts resemble the sulphates and chromates, but are much more easily hydrolyzed. The free acid resembles chloric acid (p. 483) in that, when it decomposes, it yields a higher acid ( $HMnO_4$ ) and a lower oxide ( $MnO_2$ ). The salts are green in color.

• 5. **Permanganates**,  $Mn_2O_7$ ,  $HMnO_4$  (hydrated),  $KMnO_4$ . The salts resemble the perchlorates, and are not hydrolyzed by water. They are reddish-purple in color.

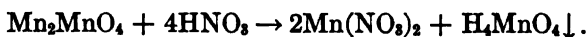


It will be seen that the element manganese changes its character totally with change in valence, and in each form of combination resembles some set of elements of valence identical with that which it has itself assumed. Since the valence represents the number of electrons gained or lost by each atom (p. 793), it is thus evident that the chemical properties of an element depend more upon the electrical constitution of its atom than upon the atomic weight. The latter is a secondary property, dependent on the former (cf. p. 470).

**Occurrence and Isolation.**—The chief ore is the dioxide, pyrolusite  $\text{MnO}_2$ , which always contains compounds of iron. Other manganese minerals are: braunite  $\text{Mn}_2\text{O}_3$ ; the hydrated form, *manganite*  $\text{MnO}(\text{OH})$ ; *hausmannite*  $\text{Mn}_3\text{O}_4$ ; and *manganese spar*  $\text{MnCO}_3$ . The last is isomorphous with calcite. The metal is most easily made by reducing one of the oxides with aluminium by Goldschmidt's method.

**Physical and Chemical Properties.**—The metal manganese (m.-p.  $1260^\circ$ ) has a grayish luster faintly tinged with red. It is oxidized superficially by air, and easily displaces hydrogen from dilute acids, giving manganous salts. Its alloys with iron, such as *spiegel iron* (5–15 per cent Mn) and *ferro-manganese* (70–80 per cent Mn), are made by using manganese ores with the charge in the blast furnace, and are added to the iron in making special steels. **Manganese steel** (7–20 per cent Mn) is exceedingly hard, even when cooled slowly. It is used for the jaws of rock crushing machinery and for burglar-proof safes. Wire, made of an alloy called *manganin* (Cu 84 per cent, Ni 4 per cent, Mn 12 per cent), invented by Weston, is used in instruments for making electrical measurements, because its resistance does not alter with moderate changes in temperature.

**Oxides.**—**Manganous oxide**  $\text{MnO}$  is a green powder, made by reducing any of the other oxides with hydrogen. **Hausmannite**  $\text{Mn}_3\text{O}_4$  is dull red. An oxide having this composition is formed when any of the other oxides is heated in air, oxidation or reduction, as the case may be, taking place (cf. p. 832). This oxide corresponds to minium  $\text{Pb}_3\text{O}_4$  (p. 832) rather than to  $\text{Fe}_3\text{O}_4$ , for with dilute acids it gives a soluble manganous salt and a precipitate of the dioxide:



The hydrated dioxide  $\text{H}_4\text{MnO}_4$  subsequently loses water. Hausmannite also forms square prismatic crystals. In view of its behavior with acids and its crystalline form, it is thought to be an orthomanganite of manganese  $\text{Mn}_2\text{MnO}_4$ , rather than a derivative of manganic oxide,  $\text{Mn}(\text{MnO}_2)_2$ , which would be a spinelle (p. 812). The magnetic oxide of iron  $\text{Fe}(\text{FeO}_2)_2$  belongs to the regular system, like the spinelles. **Manganic oxide**  $\text{Mn}_2\text{O}_3$  is brownish-black, and is formed by heating any of the oxides in oxygen. In dilute acids it behaves as if it were a manganite of manganese  $\text{Mn.MnO}_3$ , for it gives a manganous salt and manganese dioxide. Yet compounds of trivalent manganese are known, and this may be one.

**Manganese dioxide**  $\text{MnO}_2$  is black, and is most easily prepared in pure condition by gentle ignition of manganous nitrate. The hydrated forms of the oxide are produced by reactions like those just mentioned, and by adding a hypochlorite or hypobromite to manganous hydroxide suspended in water. Manganese dioxide is not a peroxidate (p. 318). That is to say, it does not contain the radical ( $\text{O}_2$ ) and, therefore, does not give hydrogen peroxide. Its reaction formula is  $\text{Mn}(\text{O})_2$  not  $\text{Mn}(\text{O}_2)$  and in double decompositions it yields only water  $\text{H}_2(\text{O})$ . In glass-making (p. 726), it is employed to oxidize the green ferrous silicate, derived from impurities in the sand, to the pale-yellow ferric compound. The amethyst color of the manganic silicate which is formed tends to neutralize this yellow. The dioxide forms the depolarizer in the Leclanché cell (p. 797). It is mixed with black paints as a "dryer" (oxidizing agent).

**Manganese trioxide**  $\text{MnO}_3$  is a red, unstable powder. **Manganese heptoxide**  $\text{Mn}_2\text{O}_7$  is a brownish-green, volatile oil (see below).

When any of these oxides is heated with an *acid*, a manganous salt is obtained. Salts of this class are, in fact, the only stable substances in which manganese is combined with an acid radical. In this action the oxides containing more oxygen than does  $\text{MnO}$  give off oxygen, or oxidize the acid (cf. p. 219). When the oxides are heated with *bases*, in the presence of air, manganates are always formed. With the oxides containing a smaller proportion of oxygen than  $\text{MnO}_3$ , oxygen is taken from the air.

**Manganous Compounds.** — The manganous salts are formed by the action of acids upon the carbonate or any of the oxides. Thus the **chloride**  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  is obtained in pale-pink crystals from a solution made by treating the dioxide with hydrochloric acid and driving off the chlorine liberated by oxidation (p. 219). The hy-

**dioxide**  $\text{Mn}(\text{OH})_2$  is formed as a white precipitate when a soluble base is added to a solution of a manganous salt. This body passes into solution when ammonium salts are added, and cannot be precipitated in their presence on account of the formation of molecular ammonium hydroxide and the suppression of the hydroxide-ion (*cf.* magnesium hydroxide, p. 766). The hydroxide quickly darkens when exposed to the air and passes over into hydrated manganic oxide  $\text{MnO}(\text{OH})$ .

**Manganous sulphate** gives pink crystals of a hydrate. Below  $6^\circ$  the solution deposits  $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ , which is a vitriol (p. 771). Between  $7^\circ$  and  $20^\circ$  the product is  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ , asymmetric and isomorphous with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Above  $25^\circ$  monosymmetric prisms of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  are obtained. These hydrates have different aqueous tensions and may be formed from one another by lowering or raising the pressure of water vapor around the substance (p. 153). The significance of the temperatures proper to the crystallization of each (*cf.* pp. 688, 728, 744) is that a given solid hydrate can be formed only in a solution which is saturated with respect to that hydrate and has the same aqueous tension as the hydrate. These conditions are necessary to that state of equilibrium between the solution and the hydrate on which the co-existence of solution and hydrate during crystallization depends (*cf.* p. 195). Hence the hydrates with the larger proportions of water, and the higher aqueous tensions, are formed in the colder solutions which contain less of the solute when saturated and have therefore at a given temperature themselves relatively high aqueous tensions.

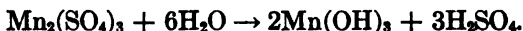
The presence of a foreign dissolved body, since it will lower the vapor tension of the solution, may similarly cause the formation of a lower hydrate. Thus, at the ordinary temperature, calcium sulphate solution has a higher aqueous tension than gypsum, and therefore gypsum is deposited from it, and anhydrite will turn into gypsum if placed in it. But calcium sulphate solution containing much of the chlorides of sodium and magnesium has a lower aqueous tension than gypsum, and so anhydrite is deposited, and gypsum in contact with such a solution would lose its water of hydration. This explains the deposition of anhydrite in the salt layers (*cf.* p. 717).

**Manganous carbonate**  $\text{MnCO}_3$  is a white powder formed by precipitation. The **sulphide**  $\text{MnS}$  is obtained as a green, crystalline powder by leading hydrogen sulphide over any of the oxides. A flesh-colored, amorphous variety  $\text{MnS}$  (often somewhat hydrated) is more familiar and is precipitated by ammonium sulphide from man-

ganous salts. It interacts with mineral acids and even with acetic acid, so that it cannot be precipitated by hydrogen sulphide (*cf.* p. 774). When rubbed in a mortar it becomes crystalline, and is then green.

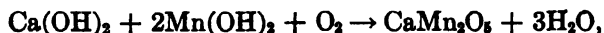
The manganous salts of weak acids, such as the carbonate and sulphide, darken when exposed to air and are oxidized, with formation of hydrated manganic oxide. As we have seen, manganous hydroxide is similarly oxidized and these salts are precisely the ones which should furnish the hydroxide by hydrolysis. While there is a general resemblance between the manganous salts and the stannous, chromous, and ferrous salts, the manganous salts of active acids are not oxidized by the air as are the corresponding salts of the other three metals.

**Manganic Compounds.** — The base of this set of compounds, **manganic hydroxide**  $\text{Mn}(\text{OH})_3$ , is slowly deposited by the action of the air on an ammoniacal solution of a manganous salt in salts of ammonium. The **chloride**  $\text{MnCl}_3$  is present in the liquid obtained by the action of hydrochloric acid upon manganese dioxide (*cf.* p. 219), but loses chlorine very readily and cannot be isolated. Double salts, however, such as  $\text{MnCl}_3 \cdot 2\text{KCl}$  and  $\text{MnF}_3 \cdot 2\text{KF} \cdot 2\text{H}_2\text{O}$ , are known. **Manganic sulphate**  $\text{Mn}_2(\text{SO}_4)_3$  is deposited as a violet-red powder when hydrated manganese dioxide is heated with concentrated sulphuric acid at  $160^\circ$ . It is deliquescent and is rapidly hydrolyzed in the cold even by a little water, giving the brownish-black hydroxide:



The **caesium-manganic alum**  $\text{Cs}_2\text{SO}_4 \cdot \text{Mn}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  seems to be the most stable derivative.

**Manganites.** — Although manganese dioxide interacts when fused with potassium hydroxide, simple salts derived from  $\text{H}_2\text{MnO}_3$  ( $= \text{H}_2\text{O} \cdot \text{MnO}_2$ ) or  $\text{H}_4\text{MnO}_4$  ( $= 2\text{H}_2\text{O} \cdot \text{MnO}_2$ ) are not formed. The products are complex, as  $\text{K}_2\text{Mn}_5\text{O}_{11}$ . Some less complex manganites are formed in the **Weldon process** for utilizing the manganous chloride, formerly obtained in manufacturing chlorine. The liquor is mixed with slaked lime, and air is blown through the mass of calcium and manganous hydroxides which is thus obtained. Black manganites of calcium, such as  $\text{CaMnO}_3$  ( $= \text{CaO} \cdot \text{MnO}_2$ ) and  $\text{CaMn}_2\text{O}_5$  ( $\text{CaO} \cdot 2\text{MnO}_2$ ) are thus formed:

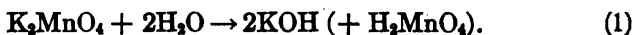


and when afterwards treated with hydrochloric acid they behave like mixtures of manganese dioxide and calcium oxide. As we have seen (p. 877), the oxides  $Mn_3O_4$  and  $Mn_2O_3$  may be manganites of manganese.

**Manganates.** — When one of the oxides of manganese is fused with potassium carbonate (or other alkali) and potassium nitrate (or other oxidizing agent) a green mass is obtained. The green aqueous extract deposits **potassium manganate**  $K_2MnO_4$  in rhombic crystals, which are isomorphous with those of potassium sulphate, and are almost black:



The acid  $H_2MnO_4$ , itself unknown, must be weak, for the potassium salt is easily hydrolyzed. The salt remains unchanged in solution only in presence of free alkali, the hydroxide-ion of the alkali combining with and suppressing the hydrogen-ion of the water whose combination with the  $MnO_4^-$  ion constitutes the hydrolysis. When the concentration of the hydroxide-ion is reduced by dilution, or, better still, when a weak acid such as carbonic acid or acetic acid is used to neutralize it, the salt is hydrolyzed, according to the partial equation:



The free acid immediately changes so that a part is oxidized to permanganic acid, giving a purple-red color to the solution, and a part is reduced to manganese dioxide, giving a black precipitate. The transformation is similar to that of chloric acid (p. 483). The equation may be made by noting that manganic acid has the composition  $H_2O, MnO_3$  and changes so as to yield  $H_2O, Mn_2O_7$  and  $MnO_2$ . Thus each molecule of  $H_2MnO_4$ , in forming a molecule of  $MnO_2$ , yields one unit of oxygen, while  $2(H_2O, MnO_3) + O$  are required to give  $H_2O, Mn_2O_7 + H_2O$ :



In consequence of the presence of potassium hydroxide (equation (1)) the product is potassium permanganate:

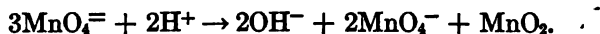


Multiplying equation (1) by 3, omitting the manganic acid, and

adding the three partial equations, we have the equation for the action as it really occurs:

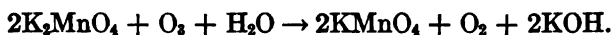


To make the equation by the method of positive and negative values (p. 493), we note that in  $\text{K}_2\text{MnO}_4$  we have  $2\text{K}^+$  and  $4\text{O}^-$  and therefore  $\text{Mn}^{++}$  to secure electrical neutrality. The latter becomes  $\text{Mn}^{+++}$  and  $\text{Mn}^{++}$ . Arithmetically  $3\text{Mn}^{++}$  will give  $2\text{Mn}^{+++}$  and  $1\text{Mn}^{++}$ . Hence,  $3\text{K}_2\text{MnO}_4$  are required, and  $2\text{KMnO}_4$  and  $1\text{MnO}_2$  produced. In terms of the ions the equation is simpler:

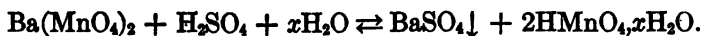


The alkaline solution of potassium manganate interacts readily with oxidizable substances. Thus oxalic acid is converted into carbonic acid, and alcohol into acetic acid. The details of the change depend upon the amount of free alkali present and the nature of the product of oxidation. Lower oxides of manganese such as  $\text{MnO}_2$  are usually precipitated.

**Permanganates.** — Potassium permanganate  $\text{KMnO}_4$  is made by hydrolysis of the manganate as shown above, and is obtained, as purple crystals with a greenish luster, by evaporation of the solution. The crystals are rhombic prisms, isomorphous with potassium perchlorate. To avoid the loss of manganese thrown down as dioxide, the action is carried out commercially by passing ozone through the solution of the manganate:



**Sodium permanganate**  $\text{NaMnO}_4$  is made in a similar manner. It is not obtainable in solid form, but its solution is known as "Condy's disinfecting fluid." This liquid owes its properties to the oxidizing power of the salt. **Permanganic acid** is a very active acid, that is, it is highly ionized in aqueous solution. A solid hydrate of the acid may be secured in reddish-brown crystals by adding sulphuric acid to a solution of barium permanganate and allowing the filtrate to evaporate:

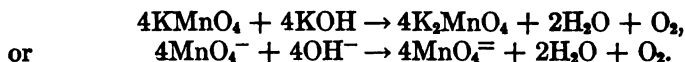


This hydrate decomposes, on being warmed to  $32^\circ$ , and yields oxygen and manganese dioxide. When a very little dry, powdered potassium permanganate is moistened with concentrated sulphuric acid, brown-

ish-green, oily drops of **permanganic anhydride** (manganese heptoxide)  $\text{Mn}_2\text{O}_7$  are formed. This compound is volatile, giving a violet vapor, and is apt to decompose explosively into oxygen and manganese dioxide. Its oxidizing power is such that combustibles like paper, ether, and illuminating-gas are set on fire by contact with it.

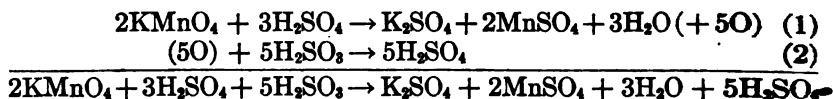
**Potassium Permanganate as an Oxidizing Agent.** — The actions are different according as the substance is employed (1) in alkaline, (2) in acid, or in neutral solution.

1. When an alkali, such as potassium hydroxide, is added, the action by which the permanganate is formed is reversed, and the solution becomes green from the production of the manganate:

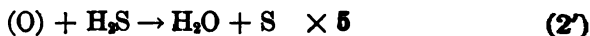


When a substance capable of being oxidized is present, the reduction proceeds further and manganese dioxide is precipitated. Schematically:  $\text{Mn}_2\text{O}_7 \rightarrow 2\text{MnO}_2 + 3\text{O}$ , so that two molecules of the permanganate, in alkaline solution, can furnish three chemical units of oxygen to the oxidizable body.

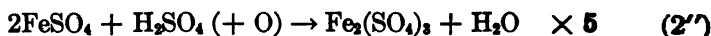
2. With an acid, the amount of oxygen available is greater, for the manganous salt of the acid is formed:  $\text{Mn}_2\text{O}_7 \rightarrow 2\text{MnO} + 5\text{O}$ . Thus when sulphuric acid is added to potassium permanganate solution, and sulphur dioxide is led through the mixture, we have:



In this case, since sulphuric acid is a product, the preliminary addition of the acid was superfluous. In other cases, the partial equation (1), showing the available 5O, remains the same, while the other partial equation varies with the substance being oxidized. Thus, with hydrogen sulphide as reducing agent, we have:



and with ferrous sulphate, we get ferric sulphate:



As before, (2') and (2'') must be multiplied throughout by five, before summation is made (see also p. 320).

Since the manganous salt is colorless, the quantity of a ferrous salt, or of hydrogen peroxide (p. 320) in a sample of a solution may be measured by titrating (p. 390) the solution with a standard solution of potassium permanganate until the color ceases to be destroyed, and then noting the volume used. For iron, the standard solution may be prepared so that 1 c.c. will oxidize 0.01 g. of  $\text{Fe}^{++}$ .

3. When dry potassium permanganate is heated, it decomposes as follows:  $2\text{KMnO}_4 \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$ . The neutral solution resembles that of potassium dichromate in oxidizing substances which are reducing agents, but is more active. Thus when the powdered salt is moistened with glycerine, the mass presently bursts into flame. The fingers are stained brown, by permanganates, receiving a deposit of manganese dioxide, in consequence of the reducing power of the unstable organic substances in the skin. The destruction of minute organisms by Condy's fluid results from a similar action.

**Analytical Reactions of Manganese Compounds.**—The ions commonly encountered are manganous-ion  $\text{Mn}^{++}$ , which is very pale-pink in color, permanganate-ion  $\text{MnO}_4^-$ , which is purple, and manganate-ion  $\text{MnO}_4^{=}$ , which is green. The manganous compounds give with ammonium sulphide the flesh-colored sulphide which interacts with acids. Bases give the white hydroxide, which darkens by oxidation, and interacts with salts of ammonium. The black, hydrated dioxide is precipitated by hypochlorites. All compounds of manganese confer upon the borax bead an amethyst color (manganic borate) which, in the reducing flame, disappears (manganous borate). A bead of sodium carbonate and niter becomes green, the manganate being formed.

**Exercises.**—1. Consider the valence of manganese in the oxides  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_4$ , on the theory that they are manganites.

2. What do we mean by saying that, (a) chromous chloride is stable (p. 148), but easily oxidized by the air, (b) permanganic acid is an active acid, (c) permanganic acid is an active oxidizing agent in presence of excess of an acid?

3. Formulate the oxidations of hydrogen sulphide, of ferrous sulphate, of oxalic acid (to carbon dioxide), and of nitrous acid (to nitric acid) by potassium permanganate in acid solution. In doing so, employ the several methods suggested on pp. 269, 493–497.



## CHAPTER XLIV

### IRON, COBALT, NICKEL

THE elements iron (Fe, at. wt. 55.84), cobalt (Co, at. wt. 58.97), and nickel (Ni, at. wt. 58.68) are not corresponding members of successive periods, like the families hitherto considered. They are neighboring members of the first long period, lying between its first and second octaves (p. 461), and form a transition group between the adjoining elements within those octaves. Thus, iron forms ferrates  $M_2Fe^{VI}O_4$  and ferric salts  $Fe^{III}Cl_3$ , as well as ferrous salts  $Fe^{II}Cl_2$ . These resemble the chromates and manganates, the chromic and manganic salts, and the chromous and manganous salts, respectively. Cobalt forms cobaltic and cobaltous salts, like  $Co_2^{III}(SO_4)_3$  and  $Co^{II}Cl_2$ . Nickel enters only into nickelous salts, like  $NiCl_2$ , and thus links iron and cobalt with copper and zinc which are both bivalent elements. The free metals of this family are magnetic, iron showing this property strongly and cobalt very distinctly.

#### IRON Fe

**Chemical Relations of the Element.** — The oxides and hydroxides  $FeO$  and  $Fe(OH)_2$ ,  $Fe_2O_3$  and  $Fe(OH)_3$  are basic, the former more strongly so than the latter. The ferrous salts, derived from  $Fe(OH)_2$ , resemble those of the magnesium group and those of  $Cr^{++}$  and  $Mn^{++}$  and are little hydrolyzed. The ferric salts, derived from  $Fe(OH)_3$ , resemble those of  $Cr^{+++}$  and  $Al^{+++}$  and are noticeably hydrolyzed. Ferric hydroxide is even less acidic, however, than is chromic hydroxide. Iron gives also a few ferrates  $K_2FeO_4$ ,  $CaFeO_4$ , etc., derived from an acid  $H_2FeO_4$  which, like manganic acid  $H_2MnO_4$ , (p. 880), is too unstable to be isolated. Complex anions containing this element, such as the anion of  $K_4Fe(CN)_6$ , are familiar, but complex cations containing ammonia are unknown.

The ferrous salts differ from most of the manganous salts and resemble the chromous and stannous salts in being easily (although not quite so easily) oxidized by the air, passing into the ferric condition.

**Occurrence.** — Free iron is found in minute particles in some basalts, and many meteorites are composed of it. Meteoric iron can be distinguished from specimens of terrestrial origin by the fact that it contains 3–8 per cent of nickel. The chief ores of iron are the oxides, hæmatite  $\text{Fe}_2\text{O}_3$  and magnetite  $\text{Fe}_3\text{O}_4$ , and the carbonate  $\text{FeCO}_3$ , siderite. The first is reddish and columnar in structure; but black, shining, rhombohedral crystals, known as specularite, are also found. Hydrated forms, like brown iron ore  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , are also common. Siderite is pale-brown in color and rhombohedral, isomorphous with calcite. When mixed with clay it forms iron-stone and, with 20–25 per cent of coal in addition, black-band. Most of the iron in Great Britain, but less than one per cent of that in the United States is obtained from these two sources. Pyrite  $\text{FeS}_2$  consists of golden-yellow, shining cubes or pentagonal dodecahedra. It is used, on account of its sulphur, in the manufacture of sulphuric acid, but, from the oxidized residue, iron of sufficient purity is obtained with difficulty. Compounds of iron are associated with chlorophyll and are found in the blood (hæmoglobin), and doubtless play an important part in connection with the vital functions of these substances. By interaction with organic compounds of iron present in the tissues, ammonium sulphide blackens the skin, ferrous sulphide being formed.

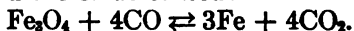
**Pure Iron.** — Pure iron is obtained by reducing pure ferrous oxalate in a stream of hydrogen at a high temperature. It is also made by electrolysis of ferrous sulphate solution at  $100^\circ$  between iron electrodes. It is silver-white and melts at  $1510^\circ$ . The purest iron does not rust in pure cold water, but the impurities in ordinary iron act as contact agents and rusting proceeds.

**Metallurgy.** — The ores of iron are first roasted in order to decompose carbonates and oxidize sulphides if these salts are present. Coke is then used to reduce the oxides. Coal is unsuitable because so much heat is wasted in driving out the volatile matter and moisture, which are absent from coke. Ores containing lime or magnesia are mixed with an acid flux, such as sand or clay-slate, in order that a fusible slag may be formed. Conversely, ores containing silica and clay are mixed with limestone. With proper adjustment of the ingredients the process can be carried on *continuously* in a blast furnace (Fig. 164), an iron structure 40 to 100 feet high, lined with firebrick. The solid materials thrown in at the top are converted, as they slowly descend, completely into gases which escape and liquids (iron and

slag) which are tapped off at the bottom. Heated air is blown in at the bottom through tuyères, and the top is closed by a cone which descends for a moment when an addition is made to the charge.

The gases, which contain much carbon monoxide, are led off and used to heat the blast or to drive gas-engines.

The main action takes place between the carbon monoxide, present in consequence of the excess of carbon, and the oxide of iron:



Since the action is a reversible one, a large excess of carbon monoxide is required. At 650°, equilibrium is reached with  $\text{CO} : \text{CO}_2 :: 1 \text{ vol.} : 1\frac{1}{2} \text{ vols.}$  at 800°, 1 vol. : 13 vols., and in practice the proportion of carbon monoxide used is from twice to fifteen times as great. Almost 5 tons of air, heated in advance to 800°, are required for each ton of iron produced. The moisture in this air acts upon the coke, giving water-gas (p. 577). This action uses up fuel, and also lowers the temperature at

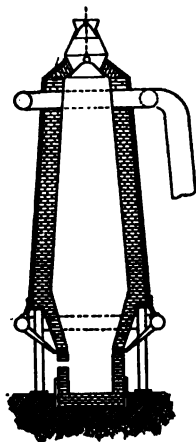


FIG. 164.

the point where it should be highest. In some plants the Gayley dry blast process was used for a time, but careful regulation of the blast, in accordance with the humidity of the air, is now the prevailing practice. In the United States alone 31 million tons of pig iron are annually produced (1913). This is considerably over 40 per cent of the world's production, 20 per cent being supplied by Germany and 15 per cent by Great Britain.

In the upper part of the furnace, the heat (400°) loosens the texture of the ore. Further down, the temperature is higher (500–900°), and the carbon monoxide reduces the oxide of iron to particles of soft iron. A temperature high enough to melt pure iron is barely reached anywhere in the furnace, but, a little lower down, by union with carbon, the more fusible cast iron (m.-p. about 1200°) is formed and falls in drops to the bottom. It is in this region also that the slag, essentially a glass, is produced. If the flux had begun sooner to interact with the unreduced ore, iron would have been lost by the formation of the silicate. The iron collects below the slag, and the latter flows continuously from a small hole. The former is tapped off at intervals of six hours or so from a lower opening. As a rule, the iron never cools until it has been converted into rails or structural iron. In some cases, it is made into "pigs" in a casting machine.

**Cast Iron and Wrought Iron.**—Pure iron is not manufactured, and indeed would be too soft for most purposes. Piano-wire, however, is about 99.7 per cent pure. The product obtained from the blast furnace contains 92–94 per cent of iron along with 2.6–4.3 per cent of carbon, often nearly as much silicon, varying proportions of manganese, and some phosphorus and sulphur. The last four ingredients are liberated from combination with oxygen by the carbon in the hottest part of the furnace and combine or alloy themselves with the iron. Cast iron does not soften before melting, as does the purer wrought iron, but melts sharply at 1150–1250° according to the amount of foreign material it contains. When *suddenly* cooled it gives **chilled cast iron** which is very brittle and looks homogeneous to the eye, all the carbon being present in the form of carbide of iron  $\text{Fe}_3\text{C}$  (cementite) in solid solution in the metal. By slower cooling, time is permitted for the separation of part of the carbon as graphite, which appears in tiny black scales (see below), and **gray cast iron** results. This mixture is much softer, on account of the amount of free, relatively pure iron which it contains.

**Wrought iron**, invented by Henry Cort (1784), is made by heating the broken “pigs” of cast iron upon a layer of material containing oxide of iron and hammer-slag (basic silicate of iron) spread on the bed of a reverberatory furnace (Fig. 143, p. 686). The carbon, silicon, and phosphorus combine with the oxygen of the oxide, and the last two pass into the slag. The sulphur is found in the slag as ferrous sulphide. On account of the effervescence due to the escape of carbon monoxide, the process is called “pig-boiling.” The iron is stirred with iron rods (“puddled”) and stiffens as it becomes purer, until finally it can be withdrawn in balls (“blooms”) and be partially freed from slag by rolling. The resulting bars are repeatedly cut, piled in a bundle, reheated, and rolled. The iron now softens sufficiently for welding below 1000° and melts at 1505° or lower, according to its purity. If it still contains more than a trace of combined phosphorus it is brittle when cold (“cold short”). A little surviving sulphide of iron makes it brittle when hot (“red-short”) and unsuitable for forging. Wrought iron should contain only 0.1–0.2 per cent of carbon. Its fibrous structure is due partly to the films of slag which have not been completely pressed out by the rolling. On account of its toughness, wrought iron is **used** for anchors, chains, and bolts, and for drawing into wire. On account of its relative purity (99.8–99.9 per cent), it is less fusible than cast iron and is used for fire bars. The above operations are now performed by machinery,

but have been largely displaced by the Bessemer and open hearth processes in which iron of equal purity can be obtained.

**Properties of Steel.**—This is a variety of iron almost free from phosphorus, sulphur, and silicon. Tool-steel contains 0.9–1.5 per cent of carbon, structural steel only 0.2–0.6 per cent, and mild steel 0.2 per cent or even less. Steel combines the properties of cast and of wrought iron, being hard and elastic, and at the same time available for forging and welding when the proportion of carbon is low. Steel can be tempered (see below). It has also a greater tensile strength\* than has wrought iron, and it can be permanently magnetized.

**Bessemer Process.**—Steel is made largely by the Bessemer process (Kelly 1852, Bessemer 1855). The molten cast iron is poured into a converter (Fig. 165) and a blast of air (*a*) is blown through it.

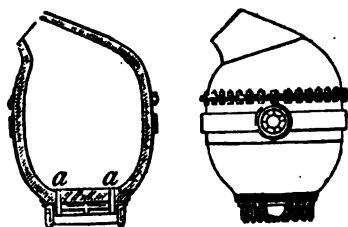


FIG. 165.

The oxidation of the manganese, carbon, silicon, and a little of the iron gives out sufficient heat to raise the temperature of the mass above the melting-point of wrought iron. The required proportion of carbon is then introduced by adding pure cast iron, spiegel iron, or coke, and the contents, first the slag, and then the molten steel, are finally poured out by turning the converter. When the cast iron contains much phosphorus, the oxide of this element is reduced again by the iron as fast as it is formed by the blast. In such cases a basic lining containing lime and magnesia takes the place of the sand and clay lining of the ordinary Bessemer converter, and a slag containing a basic phosphate of calcium is produced. This modification constitutes what is known as the **Thomas-Gilchrist process**. The slag (Thomas-slag) when pulverized forms a valuable fertilizer (cf. p. 720). In the United States, the basic open-hearth process is preferred.

Being obtained from molten material, steel and cast iron are free from slag.

\* **Tensile strength** or **tenacity** is measured by the weight (in kilos) required to break a wire of the metal 1 sq. mm. in section. Lead 2.6, copper 51, iron 71, steel 91.

**Open-Hearth (Siemens-Martin) Process.**— In this process the cast iron is melted in a saucer-shaped depression (Fig. 166), which is lined with sand in the acid process, and with lime and magnesia in the basic process. Scraps of iron plate (for dilution) and hæmatite, or some other oxide ore, are then added in proper proportions. The materials (50–75 tons in one charge) are heated with gas fuel for 8–10 hours. To secure economically the high temperature required to keep the product (almost pure iron) fused, Siemens devised the method of preheating the fuel gas and air by a regenerative device.

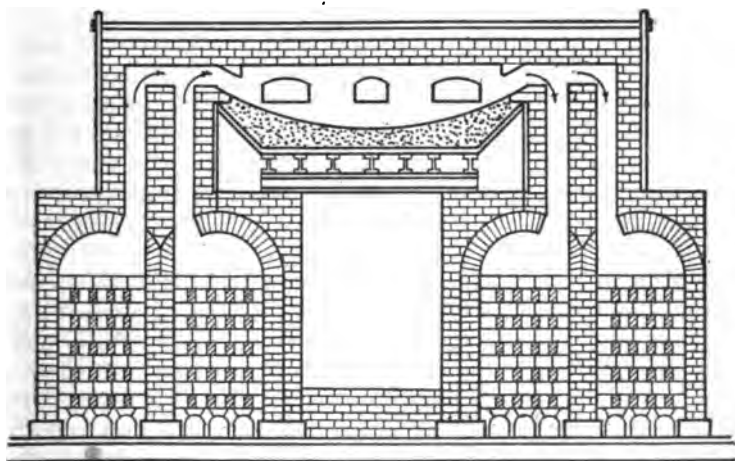


FIG. 166.

The spent air and gas pass down through a checkerwork of brick. When this becomes heated, the valves are reversed, the gas and air now enter through the heated brickwork and, after meeting and burning over the iron, pass out through the checkerwork on the opposite side, raising its temperature in turn.

The changes are similar to those in the Bessemer process. During casting, some aluminium is added to combine with oxygen (present as CO) and give sounder ingots. Recently, iron containing 10–15 per cent of titanium has been added instead. The titanium combines with both nitrogen and oxygen and the compounds pass into the slag, just as does aluminium oxide. Rails made of steel purified with this element are less liable to breakage (the commonest cause of wrecks) and are 40 per cent more durable than are ordinary open-hearth rails.

The advantage of the open-hearth process over that of Bessemer is that it is not hurried, and is therefore under better control. The material can be tested by sample at intervals until the required composition has been reached. The produce is of more uniform quality. When fine steel is required, electric heating (*e.g.*, in the Héroult furnace) permits even more deliberate treatment.

Bessemer and open-hearth steels are used for heavy and light machinery castings and for shafts. It is rolled into rails, and into bridge and structural iron.

**Crucible Steel.**—For special purposes steel is made in crucibles of clay (or graphite and clay) in melts of 60–100 pounds. “Melting bar,” a very pure open-hearth steel, is melted with charcoal or with pure pig iron. This steel is employed in making razors (1.5 per cent C), tools (1 per cent C), dies (0.75 per cent C), pens, needles, and cutlery. Special steels, containing one or more of the elements manganese, nickel, chromium, tungsten, molybdenum, and vanadium are made in this way.

**Tempering.**—When steel is heated to redness and cooled slowly, it is comparatively soft. Sudden chilling, however, renders it harder than glass. By subsequent, cautious heating the hardness may be reduced to any required extent, and this treatment is called **tempering**. The sufficiency of the heating is judged roughly by the interference colors caused by the thin film of oxide which forms on the surface. Thus a pale-yellow color (200–220°) serves for tempering razors, a decided yellow (240°) for pen-knives, a brown (260°) for shears, a purple (275°) for table-knives, a blue (300–315°) for watch-springs and sword-blades, and a black-blue (340°) for saws. Except in the case of watch-springs, these films are afterwards removed by the grinding.

To understand this behavior it must be noted that there are three states of solid iron resembling the rhombic and monoclinic states of sulphur (*cf.* p. 412). The form stable below 760° is known as  $\alpha$ -ferrite (wrought iron). It is magnetic and can hold little carbide of iron in solid solution. Above 760° this changes, with absorption of heat, into  $\beta$ -ferrite which, likewise, holds little of the carbide in solution, but is not magnetic. At 900° this changes, with further absorption of heat, into  $\gamma$ -ferrite, a non-magnetic form in which the carbide is soluble. When allowed to cool, iron assumes these forms in the reverse order. If, now, a fluid solution of carbon in iron,

suitable for steel, is *suddenly chilled*, a great part of the cold mass is a supercooled solid solution of carbon in  $\gamma$ -ferrite. This solid solution is called martensite and is very hard and brittle. It is less stable at ordinary temperatures than is  $\alpha$ -ferrite, but, as is the case with yellow phosphorus (p. 551) and amorphous sulphur (p. 413), the low temperature having once been reached, transformation into the more stable form is thereafter exceedingly slow. The material is hard steel.

When the molten steel (solution of carbon in iron) is *allowed to cool so slowly* that equilibrium can be reached at every step, a complicated series of changes ensues. First the mass solidifies (at or before  $1130^{\circ}$ ) to a mixture of martensite ( $\gamma$ -ferrite with carbon in solid solution up to 2 per cent) and graphite.\* As the temperature now falls very slowly, more graphite separates until, at  $1000^{\circ}$ , 1.8 per cent remains in solution. From this point the dissolved carbide of iron (cementite  $\text{Fe}_3\text{C}$  containing 6.6 per cent of carbon) is separated. At  $670^{\circ}$  pure  $\alpha$ -ferrite also begins to appear and there remains only about 0.9 per cent carbon in solid solution. At this temperature, if sufficient time is allowed, the solid solution separates into a mixture of pure iron (87 per cent) which is soft and carbide of iron (13 per cent) which is hard. The final result is a mechanical mixture of  $\alpha$ -ferrite (wrought iron), carbide of iron, and, if the original amount of carbon was sufficiently large, graphite. These components may be recognized by making a microscopic study of a polished surface, and their formation may be followed by chilling the specimen at any desired stage. The soft iron which predominates in the product of slow cooling makes the whole soft. Heating to a high temperature and sudden chilling gives the homogeneous solid solution of carbon in  $\gamma$ -ferrite once more and restores the qualities characteristic of steel. Moderated reheating (tempering) of the chilled mass results in more or less partial accomplishment of the changes proper to slow cooling, and consequently in a more or less close approach to the condition which results from this.

The difference between the effect of rapid and slow cooling of cast iron (p. 887) can now be made clear. Rapid cooling leads to the omission of the intervening steps enumerated above and, if something like 5 or 6 per cent of carbon is present, the material turns almost completely into martensite. This is chilled cast iron. With slower cooling, much graphite separates, and the product, gray cast iron, contains much less of the carbide and much more free iron.

\* When molten cast iron, containing 3–4.5 per cent of carbon, is cooled in this fashion, the amount of graphite may be considerable.



The various changes which occur in cooling steel are retarded by the presence of foreign substances, just as, with sulphur (p. 413), foreign substances delay the change from  $S_\alpha$  to  $S_\lambda$  and permit the supercooling of the former and its appearance in the form of amorphous sulphur. Manganese, nickel, and other metals, in particular, greatly reduce the facility with which  $\gamma$ -ferrite passes into  $\beta$ - and  $\alpha$ -ferrite at  $900^\circ$  and  $760^\circ$ . Thus iron with 12 per cent of manganese, when chilled from a high temperature, contains only supercooled  $\gamma$ -ferrite and is non-magnetic. It has to be kept for hours (instead of a few minutes) at a temperature below  $760^\circ$ , say  $500$ – $600^\circ$ , before it goes over into  $\alpha$ -ferrite. Manganese is thus a valuable constituent of steel because, by favoring the survival of the  $\gamma$ -ferrite in which alone the carbon is soluble, it permits the manufacture of a homogeneous steel containing an unusually large proportion of dissolved carbon, and allows slower cooling without loss of temper (cf. p. 890).

**Steel Alloys.**—As we have seen, substances such as aluminium, titanium, and ferrosilicon are added to iron for the purpose of purifying it, and pass in combination into the slag. There are, however, regular alloys containing the foreign metal along with the iron. Thus, **manganese steel** (7–20 per cent Mn), made by adding spiegel iron or ferromanganese (p. 876) to steel, remains hard even when cooled slowly and is used for the jaws of rock-crushers and for safes. **Chromium-vanadium steel** (1 per cent Cr, 0.15 per cent Va) has great tensile strength, can be bent double while cold, and offers great resistance to changes of stress and to torsion. It is used for frames and axles of automobiles and for connecting rods. **Tungsten steel** has already been described (p. 864). **Nickel steel** (2–4 per cent Ni) resists corrosion, has a high limit of elasticity and great hardness, and is used for armor-plate, wire cables, and propeller shafts. **Invar** (36 per cent Ni) is practically non-expansive when heated within narrow limits and is used for meter-scales and pendulum rods.

**Chemical Properties of Iron.**—Although the purest iron does not rust in cold water (p. 885), ordinary iron rusts in moist air or under water. It probably rusts in water free from carbon dioxide, displacing the hydrogen-ion, but the action is greatly hastened by the presence of carbonic acid. Rust is a brittle, porous, loosely adherent coating of variable composition, consisting mainly of a hydrated ferric oxide  $3\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , which does not protect the metal below. Oil protects iron from rusting because, although oxygen

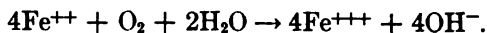
is more soluble in most oils than in water (p. 87), and so reaches the iron freely, water is not soluble in oil and so moisture is excluded.

Iron burns in oxygen and interacts with superheated steam, in both cases giving  $\text{Fe}_3\text{O}_4$ . A superficial layer of this oxide adheres firmly and protects the iron from the action of the air (Barff's process iron, or Russia iron).

Iron displaces hydrogen easily from dilute acids. Steel and cast iron, which contain iron, its carbide, and graphite, give with cold dilute acids almost pure hydrogen, and the carbide and graphite remain unattacked. More concentrated acids, however, particularly when warm, give off, along with hydrogen, hydrocarbons formed by interaction with the carbide (p. 589). The odor of the gas is due to compounds of sulphur and phosphorus. With dilute nitric acid, iron gives ferrous nitrate and ammonium nitrate (*cf.* tin, p. 824) and with the concentrated nitric acid ferric nitrate and oxides of nitrogen. Iron has little action upon alkalis.

Although iron acts vigorously on dilute or concentrated nitric acid, it is indifferent to fuming nitric acid ( $\text{NO}_2$  in solution, p. 527). It becomes **passive**. In this state, it no longer displaces hydrogen from dilute acids. If dipped in cupric sulphate solution, it does not receive the usual red coating of metallic copper. However, if scratched or struck, the passive condition is destroyed, and copper begins to be deposited at the point touched and the action spreads quickly over the whole surface. No satisfactory explanation of this phenomenon has been obtained, although it is shown also by chromium (p. 855), cobalt, and other metals.

**Ferrous Compounds.** — **Ferrous chloride** is obtained as a pale-blue hydrate  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (turning green in the air) by interaction of hydrochloric acid with the metal or the carbonate. The anhydrous salt sublimes in colorless crystals when hydrogen chloride is led over the heated metal. At a high temperature the vapor of ferrous chloride has a density corresponding to the simple formula  $\text{FeCl}_2$ , but at lower temperatures there is much association (p. 282) and the formula approaches  $\text{Fe}_2\text{Cl}_4$ . In solution the salt is oxidized by the air to a basic ferric chloride:



In presence of excess of the acid, normal ferric chloride is formed. With nitric acid, ferric chloride and nitric oxide are produced (p. 535).

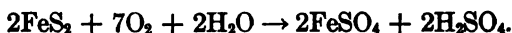
**Ferrous hydroxide**  $\text{Fe}(\text{OH})_2$  is thrown down as a white precipitate,

in water freed from dissolved oxygen by boiling, but rapidly becomes dirty-green and finally brown, by oxidation. It interacts with, and dissolves in solutions of salts of ammonium, being, like magnesium hydroxide (p. 766), sufficiently soluble in water to require an appreciable concentration of  $\text{OH}^-$  for its precipitation. The  $\text{NH}_4^+$  from the ammonium salts combines with the  $\text{OH}^-$  formed by the ferrous hydroxide to give molecular ammonium hydroxide. **Ferrous oxide**  $\text{FeO}$  is black, and is formed by heating ferrous oxalate in absence of air. It may be made also by cautious reduction of ferric oxide by hydrogen (at about  $300^\circ$ ), but is easily reduced further to the metal. It catches fire spontaneously when exposed to the air.

**Ferrous carbonate**  $\text{FeCO}_3$  is found in nature as siderite, and may be made in slightly hydrolyzed form by precipitation. The precipitate is white, but rapidly darkens and finally becomes brown, the ferrous hydroxide produced by hydrolysis being oxidized to the ferric condition. The salt interacts with water containing carbonic acid after the manner of calcium carbonate (p. 705), giving the more soluble  $\text{Fe}(\text{HCO}_3)_2$  and hence the latter is found in solution in natural (chalybeate) waters.

**Ferrous sulphide**  $\text{FeS}$  may be formed as a black, metallic-looking mass by heating together the free elements. It is produced by precipitation with ammonium sulphide, but not with hydrogen sulphide. It interacts readily with dilute acids. The precipitated form is slowly oxidized to ferrous sulphate by the air.

**Ferrous sulphate**  $\text{FeSO}_4$  is obtained by allowing pyrites to oxidize in the air and leaching the residue:



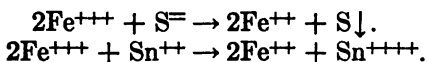
The liquor is treated with scrap iron and the neutral solution evaporated until a hydrate  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , green vitriol, or "copperas," is deposited. This substance forms green crystals belonging to the monosymmetric system, but gives also mixed crystals in which it is isomorphous with the rhombic vitriols (*cf.* Magnesium and Zinc sulphates, p. 771). The crystals are efflorescent, and also become brown from oxidation to a basic ferric sulphate:



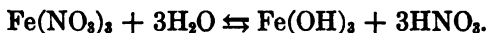
With excess of sulphuric acid and an active oxidizing agent, such as nitric acid, ferric sulphate is formed. The **double salts** of the form  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$  (Mohr's salt) are not efflorescent, and in solid form are less readily oxidized than is ferrous sulphate. The ferrous

sulphate is **used** in dyeing and in making **writing ink**. The extract of nut-galls contains tannic acid  $\text{HC}_{14}\text{H}_9\text{O}_9$ , which, with ferrous sulphate, gives ferrous tannate, a soluble, almost colorless salt. A solution of this salt containing gum-arabic and some blue or black dye constitutes the ink. When the writing is exposed to the air, the ferrous tannate is oxidized to the ferric condition, and the ferric compound is a fine, black precipitate (*cf.* p. 597). The dye is added to make the writing visible from the first. The black streaks seen below nail-heads in oak and other woods are due to the formation of ferrous carbonate and its interaction with the tannic acid in the wood. Ferrous sulphate is also used in the purification of water (p. 815).

**Ferric Compounds.** — By leading chlorine into a solution of ferrous chloride, and evaporating until the proper proportion of water alone remains, a yellow, deliquescent **hexahydrate** of **ferric chloride**,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  is obtained. When this is heated still further, hydrolysis takes place and the oxide remains. When chlorine is passed over heated iron, **anhydrous ferric chloride** sublimes in dark green scales, which are red by transmitted light. At a high temperature the formula of the vapor is  $\text{FeCl}_3$ , but at lower temperatures, in consequence of association, the density increases and the formula approaches  $\text{Fe}_2\text{Cl}_6$ . In solution, the salt, like other ferric salts, can be reduced to the ferrous condition by boiling with iron:  $2\text{Fe}^{+++} + \text{Fe} \rightarrow 3\text{Fe}^{++}$ . The same reduction is effected by hydrogen sulphide and by stannous chloride (*cf.* Mercuric chloride, p. 778):



The last action shows that ferrous salts are less active reducing agents than are the stannous salts. The ferric ion is almost colorless, the yellow-brown color of solutions of ferric salts being due to the presence of ferric hydroxide produced by hydrolysis. The color deepens when the solution is heated, and fades again very slowly, by reversal of the action, when the cold solution is allowed to stand. On the other hand, the hydrolysis may be reversed and the color may be almost destroyed, particularly in the case of the nitrate, when excess of the acid is added to the solution:



**Ferric iodide** is reduced by the hydriodic acid produced by its own hydrolysis, and hence ferrous iodide does not unite with iodine to

form this compound. The case is similar to that of cupric iodide (p. 741).

**Ferric hydroxide**  $\text{Fe}(\text{OH})_3$  appears as a brown precipitate when a base is added to a ferric salt. It does not interact with excess of the alkali. In this gelatinous form the substance dries to the oxide without giving definite intermediate hydrated oxides. The hydrates,  $\text{Fe}_4\text{O}_3(\text{OH})_6$  (brown iron ore) and  $\text{Fe}_2\text{O}(\text{OH})_4$  (bog iron ore), however, are found in nature. The hydroxide passes easily into colloidal suspension in a solution of ferric chloride, and by subsequent dialysis through a piece of parchment (*cf.* p. 621) the salt can be separated, and a pure colloidal suspension of the hydroxide obtained. This suspension, known as dialyzed iron, is red in color, shows no depression in the freezing-point, and is not an electrolyte. The hydroxide is a positive colloid and is coagulated (brown precipitate) by the addition of salts, bivalent negative ions being more effective than univalent ones (p. 844).

**Ferric oxide**  $\text{Fe}_2\text{O}_3$  is sold as "rouge" and "Venetian red." It is made from the ferrous sulphate obtained in cleaning ironware which is to be tinned or galvanized. The salt is allowed to oxidize, and the ferric hydroxide, thrown down by the addition of lime, is calcined. A purer form is produced by dry distillation of the basic ferric sulphate, an operation which used to be undertaken on a large scale for making Nordhausen sulphuric acid (p. 430). The product varies in tint from a bright yellowish-red to a dark violet-brown according to the fineness of the powder. The best rouge is obtained by calcining ferrous oxalate  $\text{FeC}_2\text{O}_4$ . This oxide is not distinctly acidic, but by fusion with more basic oxides, compounds like franklinite  $\text{Zn}(\text{FeO}_2)_2$  may be formed. It is reduced by hydrogen, at about  $300^\circ$  to ferrous oxide, and at  $700\text{--}800^\circ$  to metallic iron.

**Magnetic oxide of iron**  $\text{Fe}_3\text{O}_4$  or lodestone is found in nature, and is formed by the action of air (hammer-scale), steam, or carbon dioxide on iron. It forms octahedral crystals like the spinelles (p. 812), and is a ferrous-ferric oxide  $\text{FeO}, \text{Fe}_2\text{O}_3$  or  $\text{Fe}(\text{FeO}_2)_2$ , related to franklinite.

**Ferric sulphide**  $\text{Fe}_2\text{S}_3$  may be made by fusing together the free elements. It is obtained by precipitation when soluble sulphides are added to solutions of ferric salts (Stokes):



Formerly the precipitate was supposed to be a mixture:  $2\text{FeS} + \text{S}$ .

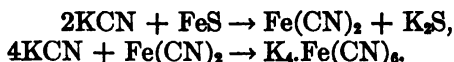
**Ferric sulphate**  $\text{Fe}_2(\text{SO}_4)_3$  is formed by oxidation of ferrous sul-

phate, and is obtained as a white mass by evaporation. It gives alums, such as  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , which are almost colorless when pure, but usually have a pale reddish-violet tinge.

**Pyrite  $\text{FeS}_2$ .** — The mineral pyrite (Fools' gold) is the sulphide of iron which is most stable in the air. It is found in nature in the form of glittering, golden-yellow cubes, octahedrons, and pentagonal dodecahedrons. It is not attacked by dilute acids, but concentrated hydrochloric acid slowly converts it into ferrous chloride and sulphur. It is reduced by hydrogen to ferrous sulphide.

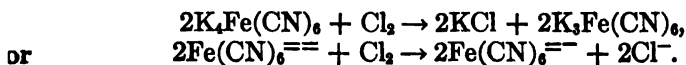
**Cyanides.** — When potassium cyanide is added to solutions of ferrous or ferric salts, yellowish precipitates are produced, but the simple cyanides cannot be obtained in pure form. These precipitates interact with excess of the cyanide giving soluble complex cyanides of the forms  $4\text{KCN} \cdot \text{Fe}(\text{CN})_2$  and  $3\text{KCN} \cdot \text{Fe}(\text{CN})_3$  respectively. These are called ferro- and ferricyanide of potassium, respectively.

**Ferrocyanide of potassium  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ ,** "yellow prussiate of potash," is made by heating nitrogenous animal refuse, such as blood, with iron filings and potassium carbonate. The resulting mass contains potassium cyanide and ferrous sulphide, and when it is treated with warm water these interact and produce the ferrocyanide:



The salt is made also from the cyanogen contained in crude illuminating-gas. The trihydrate forms large, yellow, monosymmetric tables. The solution contains almost exclusively the ions  $\text{K}^+$  and  $\text{Fe}(\text{CN})_6^{=}$ , and gives none of the reactions of the ferrous ion  $\text{Fe}^{++}$ . The corresponding acid  $\text{H}_4\text{Fe}(\text{CN})_6$  may be obtained as white crystalline scales by addition of an acid and of ether (with which the substance forms a compound or solid solution) to the salt. The acid is a fairly active one, but is unstable and decomposes in a complex manner. Other ferrocyanides may be made by precipitation. That of copper  $\text{Cu}_2\text{Fe}(\text{CN})_6$  is brown, and ferric ferrocyanide  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  has a brilliant blue color (Prussian blue). The ferrous compound (insoluble)  $\text{Fe}_2\text{Fe}(\text{CN})_6$ , or perhaps  $\text{K}_2\text{FeFe}(\text{CN})_6$ , is white, but quickly becomes blue by oxidation. The ferrocyanides are *not* poisonous.

**Ferricyanide of potassium  $\text{K}_3\text{Fe}(\text{CN})_6$**  is easily made from the ferrocyanide by oxidation:



It forms ~~real~~ monosymmetric prisms. The free acid  $\text{H}_2\text{Fe}(\text{CN})_6$  is unstable. Other salts may be prepared by precipitation. Ferrous ferricyanide  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$  is deep-blue in color (**Turnbull's blue**). With ferric salts only a brown solution is obtained.

Prussian blue and Turnbull's blue are **used** in making laundry blueing. They are insoluble, but give colloidal suspensions and are adsorbed by the material of the cloth.

**Ferric thiocyanate**  $\text{Fe}(\text{NCS})_3$  is formed by interaction of soluble thiocyanates with ferric salts (*cf.* p. 292). It is deep-red in color and gives a blood-red solution in water. Since both the ions are colorless, the solution must contain much of the molecular salt. Its formation furnishes a very delicate test for traces of ferric salts.

**Blue-Prints.** — Some ferric salts, when exposed to light, are reduced to the ferrous condition. Thus, ferric oxalate, in the light, gives ferrous oxalate:



When paper is coated with ferric oxalate solution and dried, and an ink drawing on transparent paper is placed over the prepared surface, sunlight will reduce the iron to the ferrous condition, excepting where the ink protects it. When the sheet is then dipped in potassium ferricyanide solution (developer), the ferric oxalate gives only the brown substance which can be washed out. But the deep blue, insoluble ferrous ferricyanide is precipitated in the pores of the paper where the light has acted. The drawing appears white on a blue blackground. In ordinary blue-print paper, ammonium-ferric citrate takes the place of the oxalate, and the ferricyanide has already been applied to the paper before drying, so that only exposure and washing remain to be done. Dilute sodium hydroxide solution decomposes the ferricyanide, and is used for writing (in white) on blue-prints.

**Iron Carbonyls.** — When carbon monoxide is led over finely divided iron at  $40\text{--}80^\circ$ , or under eight atmospheres pressure at the ordinary temperature, volatile compounds of the composition  $\text{Fe}(\text{CO})_5$ , **iron tetracarbonyl**, and  $\text{Fe}(\text{CO})_6$ , the **pentacarbonyl**, are formed. When the gaseous mixture is heated more strongly, the compounds decompose again, and iron is deposited. Illuminating-gas burners frequently receive a deposit of iron from this cause.

**Ferrates.** — A red solution of potassium ferrate  $K_2FeO_4$ , is obtained by passing chlorine through caustic potash in which ferric hydroxide is suspended, or by heating pulverized iron with dry sodium nitrate. The salt crystallizes in red, rhombic prisms, isomorphous with the sulphate and chromate of potassium. It alters quickly in solution, in consequence of hydrolysis and subsequent decomposition of the ferric acid, depositing ferric hydroxide and giving off oxygen. Barium, strontium, and calcium salts are formed as red precipitates by double decomposition.

**Analytical Reactions of Compounds of Iron.** — There are two ionic forms of iron, ferrous-ion  $Fe^{++}$ , which is very pale-green, and ferric-ion  $Fe^{+++}$ , which is almost colorless. The yellow color of ferric salts is due to hydrolysis. Ammonium sulphide gives with the former black ferrous sulphide, which is soluble in dilute acids. The hydroxides are white and brown respectively, and ferrous carbonate is white. With ferric salts, which are hydrolyzed (about 5 per cent), soluble carbonates yield the hydroxide, because they neutralize the free acid and displace the equilibrium. With ferrocyanide of potassium, ferrous salts give a white, and ferric salts a blue, precipitate. With ferricyanide of potassium the former give a deep-blue precipitate, and the latter a brown solution. Ferric thiocyanate is deep-red. From ferric solutions barium carbonate throws down ferric hydroxide. When sodium acetate is added in excess to a ferric salt, a red, little ionized, but easily hydrolyzed, **ferric acetate** is formed. When the solution is boiled the hydrolysis is increased, and an insoluble, basic ferric acetate is thrown down. With borax, iron compounds give a bead which is green (ferrous borate) in the reducing flame, and colorless or, with much iron, yellow (ferric borate) or even brown when oxidized.

### COBALT Co

**The Chemical Relations of the Element.** — Cobalt forms cobaltous and cobaltic oxides and hydroxides  $CoO$  and  $Co(OH)_2$ ,  $Co_2O_3$ , and  $Co(OH)_3$ , respectively, which are all basic, the former more so than the latter. The cobaltous salts are little hydrolyzed, but the cobaltic salts are largely decomposed by water. The latter also liberate readily one-third of the negative radical, after the manner of manganic salts, becoming cobaltous. Complex cations and anions containing cobalt are very numerous and very stable.



**Occurrence and Properties.**—Cobalt is found along with nickel in smaltite  $\text{CoAs}_2$  and cobaltite  $\text{CoAsS}$ . The pure metal may be made by Goldschmidt's process, or by reducing the oxalate, or an oxide, with hydrogen.

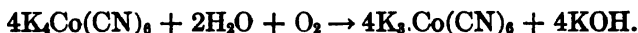
The metal is silver-white, with a faint suggestion of pink. It is less tough than iron, and has no commercial applications. It displaces hydrogen slowly from dilute acids, but interacts readily with nitric acid.

**Cobaltous Compounds.**—The chloride  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  may be made by treating the oxide with hydrochloric acid. It forms red prisms, and when partially or completely dehydrated becomes deep-blue. Writing made with a diluted solution upon paper is almost invisible, but becomes blue when warmed and afterwards takes up moisture from the air, and is once more invisible (*sympathetic ink*). Most cobaltous compounds are red when hydrated or in solution ( $\text{Co}^{++}$ ) and blue when dehydrated. The blue color assumed by a strong solution of cobaltous chloride, when it is warmed, or when hydrochloric acid is added to it, is explained by some chemists as being due to repression of the ionization of the salt, and by others as being due to the formation of the complex anion of the salt  $\text{Co}^{++} \cdot \text{CoCl}_4^-$ . By addition of sodium hydroxide to a cobaltous salt, a blue basic salt is precipitated. When the mixture is boiled, the pink **cobaltous hydroxide**,  $\text{Co}(\text{OH})_2$ , is formed. This becomes brown through oxidation by the air. It interacts with ammonium hydroxide, giving a soluble ammonio-cobaltous hydroxide (cf. p. 784), which is quickly oxidized by the air to an ammonio-cobaltic compound (see below). It interacts also with salts of ammonium as does magnesium hydroxide (p. 766). When dehydrated it leaves the black **cobaltous oxide**. **Cobaltous sulphate**  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , isomorphous with magnesium sulphate, and the **nitrate**  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  are familiar salts. The black **cobaltous sulphide**  $\text{CoS}$  is precipitated by ammonium sulphide from solutions of all salts, and even by hydrogen sulphide from the acetate, or a solution containing much sodium acetate (cf. p. 716). Once it has been formed, it does not interact even with dilute hydrochloric acid, having apparently changed into a less active form. A sort of **cobalt glass**, made by fusing sand, cobalt oxide, and potassium nitrate, forms, when powdered, a blue pigment **smalt**, used in china-painting and by artists.

**Cobaltic Compounds.**—By addition of a hypochlorite to a solution of a cobaltous salt, **cobaltic hydroxide**  $\text{Co}(\text{OH})_3$ , a bla

powder, is precipitated. Cautious ignition of the nitrate gives **cobaltic oxide**  $\text{Co}_2\text{O}_3$ . Stronger ignition gives the commercial oxide which is a **cobalto-cobaltic oxide**  $\text{Co}_3\text{O}_4$ . Cobaltic oxide dissolves in cold hydrochloric acid, but the solution gives off chlorine when warmed. By placing cobaltous sulphate solution round the anode of an electrolytic cell, crystals of **cobaltic sulphate**  $\text{Co}_2(\text{SO}_4)_3$  have been made and cobaltic alums have also been prepared (Hugh Marshall).

**Complex Compounds.** — Potassium cyanide precipitates from cobaltous salts a brownish-white cyanide. This interacts with excess of the reagent, giving a solution of **potassium cobaltocyanide**  $\text{K}_4\text{Co}(\text{CN})_6$  (cf. p. 897). This compound is easily oxidized by chlorine, or even when the solution is boiled in the air, and the colorless **potassium cobalticyanide** is formed:



The solution gives none of the reactions of  $\text{Co}^{+++}$ , and with acids the very stable cobalticyanic acid  $\text{H}_3\text{Co}(\text{CN})_3$  is liberated.

When acetic acid and potassium nitrite are added to a cobaltous salt the latter is oxidized by the nitrous acid (liberated by the acetic acid) and a yellow complex salt  $\text{K}_3\text{Co}(\text{NO}_2)_6 \cdot n\text{H}_2\text{O}$  ( $= \text{Co}(\text{NO}_2)_3 \cdot 3\text{KNO}_2$ ), **potassium cobaltinitrite**, is thrown down.

Cobaltic salts give with ammonia complex compounds which are many and various. The cations often contain negative groups, and are such as  $\text{Co}(\text{NH}_3)_6^{+++}$ ,  $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$  and  $\text{Co}(\text{NH}_3)_5\text{NO}_2^{++}$ . Usually the solutions give none of the reactions of cobaltic ions, and often fail likewise to give those of the anion of the original salt.

## NICKEL Ni

**The Chemical Relations of the Element.** — Nickel forms nickelous and nickelic oxides and hydroxides  $\text{NiO}$  and  $\text{Ni}(\text{OH})_2$ ,  $\text{Ni}_2\text{O}_3$  and  $\text{Ni}(\text{OH})_3$ , but only the former are basic. The nickelous salts resemble the cobaltous and ferrous salts, but are not oxidizable into corresponding nickelic compounds. Since there are no nickelic salts, there are here no analogues of the cobalticyanides or the cobaltinitrites. The complex nickelous salts, like the complex cobaltous salts, and unlike the complex cobaltic salts, are unstable, and so give some of the reactions of  $\text{Ni}^{++}$ .

**Occurrence and Properties.**—Nickel occurs in meteorites (free) and in niccolite  $\text{NiAs}$  and nickel glance  $\text{NiAsS}$ . It is now manufactured chiefly from pentlandite  $[\text{Ni,Cu,Fe}]_9\text{S}_{10}$  and other minerals found at Sudbury, Ontario (production in 1913, 24,840 short tons), and from garnierite, a silicate of nickel and magnesium, found in New Caledonia. In the former case, the ore is roasted, smelted, and finally bessemerized. The resulting alloy of copper and nickel is much used for sheet-metal work (**Monel metal**, approx. 1 : 1). Pure nickel is separated from the copper by an electrolytic process (p. 747), or by the Monde process (see below).

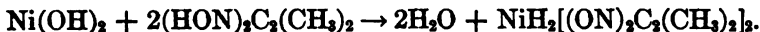
The metal is white, with a faint tinge of yellow, is very hard, and takes a high polish (m.-p.  $1452^\circ$ ). It is used in making alloys, such as German silver (copper, zinc, nickel, 2 : 1 : 1) and the "nickel" used in coinage (copper, nickel, 3 : 1). Although in these alloys the red color of the copper is completely lost, the copper is simply dissolved, and not combined. Zinc and copper, however, give a compound  $\text{Cu}_2\text{Zn}_3$ . Nickel plating on iron is accomplished exactly like silver plating (p. 755). The bath contains an ammoniacal solution of ammonium-nickel sulphate  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , and a plate of nickel forms the anode.

The metal rusts very slowly in moist air. It displaces hydrogen with difficulty from dilute acids, but interacts with nitric acid.

**Compounds of Nickel.**—The chloride  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  is made by treating one of the oxides with hydrochloric acid, and is green in color (when anhydrous, brown). The sulphate  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , which crystallizes in green, square prismatic forms at  $30\text{--}40^\circ$ , is the most familiar salt. The heptahydrate  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , obtained from cold solutions, is isomorphous with magnesium sulphate. Nickelous hydroxide  $\text{Ni}(\text{OH})_2$  is formed as an apple-green precipitate, and when heated leaves the green nickelous oxide  $\text{NiO}$ . It interacts with ammonium hydroxide, giving a complex ammonio-nickel cation. It also interacts with and dissolves in salts of ammonium (cf. p. 766). By cautious ignition of the nitrate, nickelic oxide  $\text{Ni}_2\text{O}_3$ , is formed as a black powder. The oxides and salts, when heated strongly in oxygen, give the oxide  $\text{Ni}_3\text{O}_4$ . The last two oxides liberate chlorine when treated with hydrochloric acid, and give nickelous chloride. Nickelic hydroxide  $\text{Ni}(\text{OH})_3$  is a black precipitate formed when a hypochlorite is added to any salt of nickel. Nickelous sulphide is thrown down by ammonium sulphide, and behaves like cobaltous sulphide (p. 900).

It forms a brown colloidal solution when excess of the precipitant is used, and is then deposited very slowly.

Addition of **dimethylglyoxime** to an ammoniacal solution of a salt of nickel gives a scarlet precipitate of **an acid salt**:



This reaction is not shown by salts of cobalt, especially if oxidation to the cobaltic condition has been permitted by contact with air.

With potassium cyanide and a salt of nickel the greenish **nickelous cyanide**  $\text{Ni(CN)}_2$  is first precipitated. This dissolves in excess of the reagent, and a complex salt  $\text{K}_2\text{Ni(CN)}_4 \cdot \text{H}_2\text{O}$  ( $= 2\text{KCN}, \text{Ni(CN)}_2$ ) may be obtained from the solution. This salt is of different composition from the corresponding compounds of cobalt and iron, and is less stable. Thus, with bleaching powder, it gives  $\text{Ni(OH)}_2$  as a black precipitate. When the solution is boiled in the air no oxidation to a complex nickelic cyanide occurs, and indeed no such salts are known. This fact enables the chemist to separate cobalt and nickel, for when the mixed cyanides are boiled and then treated with bleaching powder, the cobalt cyanide is unaffected. With potassium nitrite and acetic acid no insoluble compound corresponding to that given by cobalt salts is formed by salts of nickel. The only known compound which could be formed,  $4\text{KNO}_2, \text{Ni(NO}_2)_2$ , is soluble. This action also is used for the purpose of separation. The pink color of cobalt salts and the green of nickel salts are complementary colors, so that, by using suitable proportions of the two, a colorless mixture can be produced.

When finely divided nickel, made by reducing the oxide or oxalate with hydrogen at a moderate temperature, is exposed to a stream of cold carbon monoxide, **nickel carbonyl**  $\text{Ni(CO)}_4$  is formed. This is a vapor and is condensable to a colorless liquid (b.-p.  $43^\circ$  and m.-p.  $-25^\circ$ ). The vapor is poisonous. When heated to  $150\text{--}180^\circ$  it is dissociated and nickel is deposited. Cobalt forms no corresponding compound. In commerce, pure nickel is separated from copper (and cobalt) in the **Monde process** by passing carbon monoxide over the pulverized alloy, and subsequently heating the gas.

#### *Analytical Reactions of Compounds of Cobalt and Nickel.*

— Cobaltous-ion  $\text{Co}^{++}$  is pink, and the nickelous ion  $\text{Ni}^{++}$  green. The reactions used in analysis have been described in the preceding paragraphs. With borax, cobalt compounds give a blue bead (cobaltous borate), and nickel compounds a bead which is brown in the oxi-

dizing flame and cloudy, from the presence of metallic nickel, when reduced.

**Exercises.** — 1. What would be the interactions of calcium carbonate when fused with sand and with clay, respectively?

2. Make equations representing, (a) the oxidation of ferrous chloride by air, (b) the hydrolysis of ferrous carbonate and the oxidation of ferrous hydroxide, (c) the oxidation of ferrous sulphate with excess of sulphuric acid by hypochlorous acid, (d) the formation of ferrous and ferric tannates (p. 895), (e) the reduction of ferric chloride by iron, by hydrogen sulphide, and by stannous chloride, respectively, (f) the dry distillation of basic ferric sulphate, (g) the formation of ferric ferrocyanide and of ferrous ferricyanide, (h) the hydrolysis and decomposition of potassium ferrate.

3. Explain the solubility of cobaltous and nickelous hydroxides in salts of ammonium.

4. Construct equations to show the formation, (a) of the insoluble potassium cobaltinitrite (nitric oxide is given off), (b) of nickelic hydroxide from nickelous chloride and sodium hypochlorite. Remembering that the hypochlorite is somewhat hydrolyzed, explain why the precipitation in (b) is complete.

5. Tabulate in detail the chemical relations of the elements cobalt and nickel, especially to show the resemblances and differences.

## CHAPTER XLV

### THE PLATINUM METALS

THE remaining elements of Mendelejeff's eighth group divide themselves into two sets of three each. Just as iron, cobalt, and nickel have similar atomic weights and much the same density (7.8–8.8), so **ruthenium** (Ru, at. wt. 101.7), **rhodium** (Rh, at. wt. 103), and **palladium** (Pd, at. wt. 106.7) have densities from 12.26 to 11.5. Similarly **osmium** (Os, at. wt. 191), **iridium** (Ir, at. wt. 193), and **platinum** (Pt, at. wt. 195.2) form a triad with specific gravities from 22.5 to 21.5. Chemically, ruthenium shows the closest resemblance to osmium, and both are allied to iron. Similarly, rhodium and iridium, and palladium and platinum are natural pairs.

The six elements are found alloyed in nuggets and particles which are separated from alluvial sand by washing. Platinum forms 60–84 per cent of the whole. The chief deposits are in the Ural Mountains, smaller amounts being found in California, Australia, Borneo, and elsewhere. The components are separated by a complex series of chemical operations.

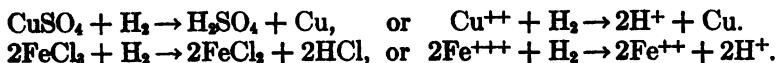
**Ruthenium and Osmium.** — These metals are gray like iron, while the other four are whiter and more like cobalt and nickel. They also resemble iron in being the most infusible members of their respective sets. Both melt considerably above 2000°. They likewise resemble iron in uniting easily with free oxygen, while the other four elements do not. Ruthenium gives  $\text{Ru}_2\text{O}$  in air, and  $\text{RuO}_2$  in oxygen. Osmium gives  $\text{OsO}_4$ , "**osmic acid**," a white crystalline body melting at 40° and boiling at about 100°. The odor and irritating effects of the vapor recall chlorine (Gk., *ὄσμη*, odor). The substance is not an acid, nor even an acid anhydride. The aqueous solution is used in histology, and stains tissues in consequence of its reduction by organic bodies to metallic osmium. It is affected particularly by fat. Osmic acid also hardens the material without distorting it. Osmium forms also a yellow, crystalline **fluoride**  $\text{OsF}_8$  (m.-p. 34.5°). Ruthenium and osmium have a maximum valence of eight.

These elements resemble iron in giving ruthenates and osmates, like  $K_2RuO_4$  and  $K_2OsO_4$ , but no corresponding oxide or acid. **Potassium ruthenate** resembles potassium manganate and gives, when diluted, an oxide of ruthenium and **potassium perruthenate**  $KRuO_4$ . There are salts derived from the oxides  $Ru_2O_3$  and  $Os_2O_3$ .

**Rhodium and Iridium.** — These metals are not attacked by *aqua regia*, while the other four are dissolved, more or less slowly. They are harder than platinum, and iridium is alloyed with this metal for the purpose of increasing its hardness (pens), and its resistance to the action of fluorine. They resemble cobalt in having no acid-forming properties. Salts corresponding to the oxides  $Rh_2O_3$  and  $Ir_2O_3$  are formed, and iridium gives compounds derived from  $IrO_2$  as well. The most familiar compounds of iridium are the **complex chlorides**  $X_3IrCl_6$  ( $= 3XCl, IrCl_6$ ) and  $X_2IrCl_6$  ( $= 2XCl, IrCl_6$ ). The solutions of the latter are red, and the acid, **chloro-iridic acid**  $H_2IrCl_6$ , is often found in commercial chloroplatinic acid  $H_2PtCl_6$ , and confers upon it a deeper color.

**Palladium and Platinum.** — Palladium is the only metal of this family which is attacked by nitric acid. Palladium and platinum forms *-ous* and *-ic* compounds of the forms  $PdX_2$  and  $PdX_4$ , respectively. The oxides  $PdO$  and  $PtO$  and the corresponding hydroxides are basic. When quadrivalent, the metals appear chiefly in complex compounds, like  $H_2PtCl_6$ ,  $H_2PdCl_6$ , in which the metal is in the anion. Platinum gives also platينات derived from the oxide  $PtO_2$ , and quadrivalent platinum furnishes no well defined salts in which it constitutes by itself the positive ion.

**Palladium.** — This metal (m.-p.  $1549^\circ$ ), named from the planetoid Pallas, is noted chiefly for its great tendency to absorb hydrogen. When finely divided, it takes up about 800 times its own volume. The amount absorbed varies continuously with the concentration (pressure) of the hydrogen, although not according to a uniform rule, and the product is in part at least a solid solution. When a strip of palladium is made the cathode of an electrolytic cell, over 900 volumes of hydrogen may be occluded. This absorbed hydrogen, in consequence of the catalytic influence of the metal, reacts more rapidly than does the gas, and consequently a strip of hydrogenized palladium will quickly precipitate copper and other metals less electro-positive than hydrogen and will reduce ferric and other reducible salts:



The **palladious salts** are such as  $\text{PdCl}_2$ ,  $\text{PdSO}_4$ ,  $\text{Pd}(\text{NO}_3)_2$ . Palladic chloride, formed by treating the metal with *aqua regia*, is contained in the solution in the form of chloropalladic acid  $\text{H}_2\text{PdCl}_6$  ( $= 2\text{HCl}, \text{PdCl}_4$ ) and gives difficultly soluble salts like  $\text{K}_2\text{PdCl}_6$ . When the solution of the acid is boiled, however, chlorine is given off and  $\text{PdCl}_2$  or  $\text{H}_2\text{PdCl}_4$  remains in solution.

**Platinum.** — This metal (dim. of Sp. *plata*, silver) is grayish-white in color, and is very ductile. At a red heat it can be welded. It does not melt in the Bunsen flame, but fuses easily in the oxyhydrogen jet (m.-p.  $1755^\circ$ ). On account of its very small chemical activity it is used in electrical apparatus and for making wire, foil, crucibles and other vessels for use in laboratories. It unites, however, with carbon, phosphorus, and silicon, becoming brittle, and forms fusible alloys with metals like antimony and lead. Hence care has to be taken not to heat in vessels made of it compounds from which these elements may be liberated. It also interacts with fused alkalis, giving platinates, but the alkali carbonates may be melted in vessels of platinum with impunity. The oxygen acids are without action upon it, but on account of the tendency to form the extremely stable complex ion  $\text{PtCl}_6^-$  (p. 537), the free chlorine and chloride-ion in *aqua regia* convert it into chloroplatinic acid  $\text{H}_2\text{PtCl}_6$ .

The metal condenses oxygen upon its surface and it dissolves hydrogen. The finely divided forms of the metal, such as **platinum sponge** made by igniting ammonium chloroplatinate  $(\text{NH}_4)_2\text{PtCl}_6$ , and **platinum black** made by adding zinc to chloroplatinic acid, show this behavior very conspicuously. They cause instant explosion of a mixture of oxygen and hydrogen, in consequence of the heat developed by the rapid union of that part of the gases which is condensed in the metal. A heated spiral of fine platinum wire will continue to glow if immersed in the mixture of alcohol vapor and air (oxygen) formed by placing a little alcohol in a beaker. Some cigar-lighters work on this principle. The heat is developed by the interaction between the substances, which takes place with great speed at the surface of the platinum (*cf.* p. 596).

Platinum is the only otherwise suitable single substance which has the same coefficient of expansion as glass, and it was consequently fused into incandescent bulbs and furnished the electrical connection



with the filament in the interior. Recently it has been displaced by Eldred's wire, containing a core of nickel steel with a jacket of copper and an outer sheath of platinum. This shrinks slightly less than does glass on cooling. Large amounts are also consumed in photography and by dentists. It is used in making jewelry, and in Russia for coinage. The price of the metal is very variable, since a rainy season in the Caucasus will render larger amounts accessible to the miners, but, on the whole, the many applications which have been found for it have quintupled its price in the last twenty years.

**Compounds of Platinum.** — **Platinous chloride**  $\text{PtCl}_2$  is made by passing chlorine over finely divided platinum at  $240\text{--}250^\circ$  or by heating chloroplatinic acid to the same temperature. It is greenish and insoluble in water, but forms with hydrochloric acid the soluble **chloroplatinous acid**  $\text{H}_2\text{PtCl}_4$ . Potassium chloroplatinite  $\text{K}_2\text{PtCl}_4$  is used in making platinum prints (*cf.* p. 757). Bases precipitate black **platinous hydroxide**  $\text{Pt}(\text{OH})_2$  which interacts with acids but not with bases. Gentle heating gives the **oxide**  $\text{PtO}$  and stronger heating the metal. With potassium cyanide and barium cyanide soluble **platino-cyanides**,  $\text{K}_3\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$  and  $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ , are formed. These substances, when solid, show strong fluorescence, converting X-rays as well as ultra-violet rays into visible radiations. The barium salt is used on screens to receive the shadows cast by X-rays.

**Platinic chloride**  $\text{PtCl}_4$  may be made by treating the metal with *aqua regia* and heating the **chloroplatinic acid**  $\text{H}_2\text{PtCl}_6$  so formed in a stream of chlorine at  $360^\circ$ . When dissolved in water, however, it gives a compound  $\text{H}_2\text{PtCl}_6\text{O}$  in which platinum is in the anion. Its solution deposits red, non-deliquescent crystals of  $\text{H}_2\text{PtCl}_6\text{O} \cdot 4\text{H}_2\text{O}$ .

**Chloroplatinic acid** forms reddish-brown deliquescent crystals  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ . With potassium and ammonium salts, it yields the sparingly soluble, yellow chloroplatinates  $\text{K}_2\text{PtCl}_6$  and  $(\text{NH}_4)_2\text{PtCl}_6$  (*cf.* p. 677), in solutions of which the platinum migrates towards the anode and silver salts precipitate  $\text{Ag}_3\text{PtCl}_6$  and not silver chloride.

Bases interact with chloroplatinic acid, giving a yellow or brown precipitate of **platinic hydroxide**  $\text{Pt}(\text{OH})_4$ . This substance interacts both with acids and with bases. In the latter case **platinates**, like  $\text{Na}_2\text{H}_{10}\text{Pt}_3\text{O}_{12} \cdot \text{H}_2\text{O}$ , have been obtained. Both sets of platinum compounds interact with hydrogen sulphide, giving the **sulphides**,  $\text{PtS}$  and  $\text{PtS}_2$ . These are black powders which interact with yellow ammonium sulphide solution giving ammonium sulphoplatinates.

## APPENDIX

### I. The Metric System

**Length.** 1 meter (1 m.) = 10 decimeters = 100 centimeters (100 cm.) = 1000 millimeters (1000 mm.).

1 kilometer = 1000 meters (1000 m.).

1 decimeter = 0.1 m. = 10 centimeters = 3.937 inches.

1 meter = 1.094 yards = 3.286 ft. = 39.37 inches.

**Volume.** 1 liter = 1000 cubic centimeters (1000 c.c.) = a cube 10 cm.  $\times$  10 cm.  $\times$  10 cm.

1 liter = 0.03532 cu. ft. = 61.03 cu. in. = 1.057 quarts (U. S.) or 1.136 quarts (Brit.) = 34.1 fl. oz. (U. S.) = 35.3 oz. (Brit.).

1 fl. ounce (U. S.) = 29.57 c.c. 1 ounce (Brit.) = 28.4 c.c.

1 cu. ft. = 28.32 liters.

**Weight.** 1 gram (g.) = wt. of 1 c.c. of water at 4° C. 1 kilogram = 1000 g.

1 gram = 10 decigrams = 100 centigrams (100 cgm.) = 1000 milligrams (1000 mgm.).

1 kilogram = 2.205 lbs. avoird. (U. S. and Brit.).

1 lb. avoird. = 453.6 g.

1 oz. avoird. (U. S. and Brit.) = 28.35 g. 100 g. = 3.5 oz.

1 nickel (U. S.) weighs 5 g. 1 halfpenny (Brit.), 5 to 5.7 g.

1 long ton = 2240 lbs. 1 short ton = 2000 lbs. 1 metric ton = 1000 kilos = 2205 lbs.

### II. Scale of Hardness

Each of the following minerals will scratch the surface of a specimen of any one *preceding* it in the list.

- |                     |             |
|---------------------|-------------|
| 1. Talc             | 6. Felspar  |
| 2. Gypsum (or NaCl) | 7. Quartz   |
| 3. Calcite (or Cu)  | 8. Topaz    |
| 4. Fluorite         | 9. Corundum |
| 5. Apatite          | 10. Diamond |

**Glass** is slightly scratched by 5, and easily by those following.

**Glass** will not scratch 5 distinctly, but will scratch those preceding 5.

A good **knife** scratches 6 slightly, but not those following.

A **file** will scratch 7, but not those following.

### III. Temperatures Centigrade and Fahrenheit

Upon the centigrade scale, the freezing-point of water is  $0^{\circ}$  C. and the boiling-point  $100^{\circ}$  C. Upon the Fahrenheit scale, the same points are  $32^{\circ}$  F. and  $212^{\circ}$  F., respectively. The same interval is thus  $100^{\circ}$  on the one scale and  $180^{\circ}$  on the other. The degree Fahrenheit is therefore  $\frac{9}{5}$  or  $\frac{5}{9}$  of  $1^{\circ}$  Centigrade. Any temperatures can be converted by using the formulæ:

$$C.^{\circ} = \frac{5}{9} (F.^{\circ} - 32), \quad F.^{\circ} = \frac{9}{5} (C.^{\circ}) + 32.$$

The following table (IV) contains the temperatures from  $0^{\circ}$  C. to  $35^{\circ}$  C., with the corresponding values on the Fahrenheit scale ( $32^{\circ}$  F. to  $95^{\circ}$  F.).

### IV. Vapor Pressures of Water

Both the Fahrenheit (F.) or ordinary and the Centigrade (C.) temperatures are given.

Temperature.		Pressure, mm.	Temperature.		Pressure, mm.
F.	C.		F.	C.	
32°	0°	4.6	71.6°	22°	19.7
41	5	6.5	73.4	23	20.9
46.4	8	8.0	75.2	24	22.2
48.2	9	8.6	77.0	25	23.6
50.0	10	9.2	78.8	26	25.1
51.8	11	9.8	80.6	27	26.5
53.6	12	10.5	82.4	28	28.1
55.4	13	11.2	84.2	29	29.8
57.2	14	11.9	86.0	30	31.5
59.0	15	12.7	87.8	31	33.4
60.8	16	13.5	89.6	32	35.4
62.6	17	14.4	91.4	33	37.4
64.4	18	15.4	93.2	34	39.6
66.2	19	16.3	95.0	35	41.8
68.0	20	17.4	.....	.....	.....
69.8	21	18.5	212.0	100	760.0

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\*.\* Acids are all listed under "acid," and salts under the positive radical.

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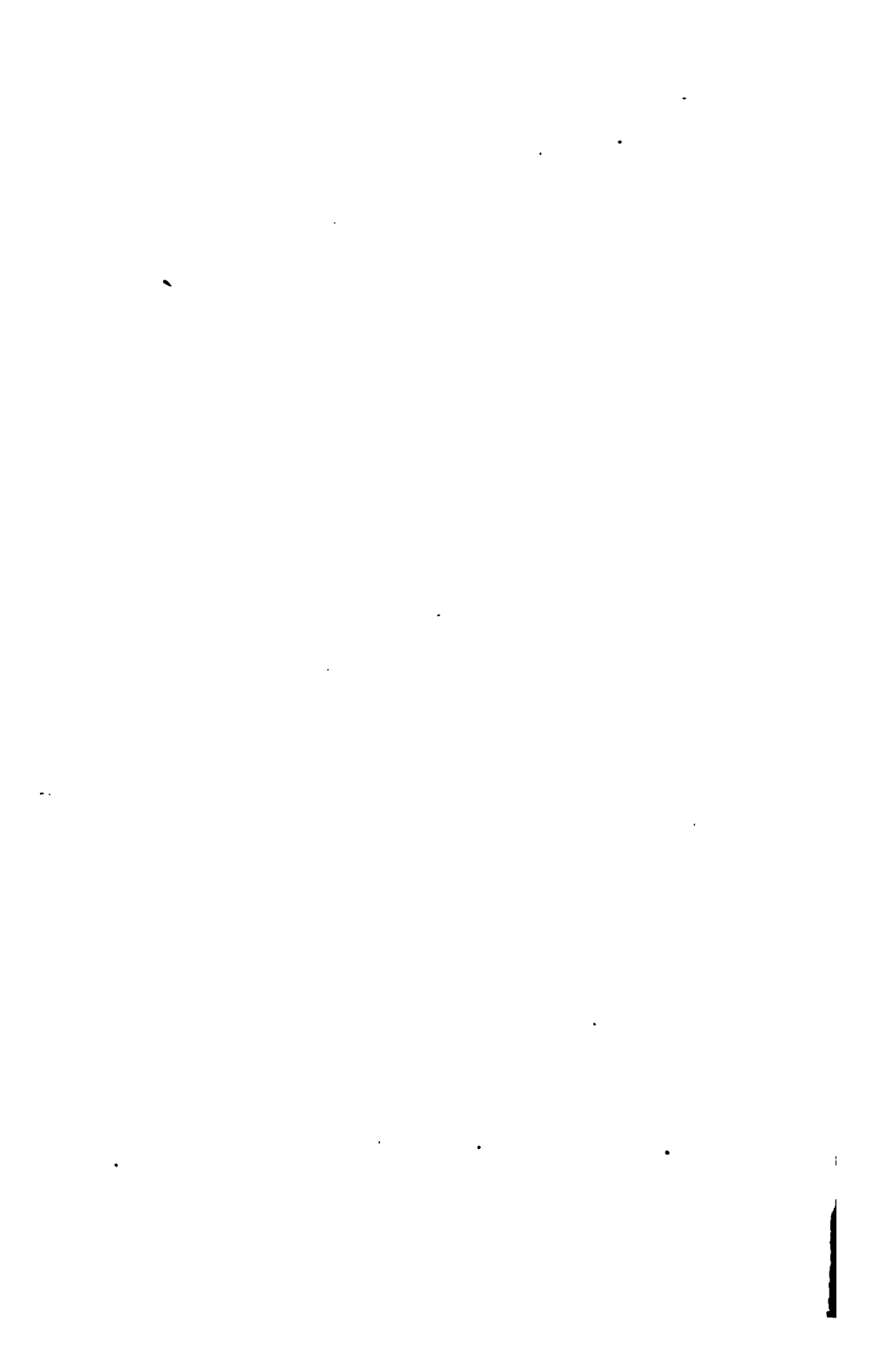




TABLE OF THE PERIODIC SYSTEM

E°	E <sup>ICl</sup> E <sub>1</sub> O	E <sup>ICl</sup> <sub>2</sub> E <sub>2</sub> O	E <sup>III</sup> Cl <sub>3</sub> E <sub>3</sub> HO <sub>3</sub>	E <sup>IV</sup> H <sub>4</sub> E <sup>IV</sup> O <sub>2</sub>	E <sup>III</sup> H <sub>3</sub> E <sub>3</sub> O <sub>3</sub>	E <sup>II</sup> H <sub>2</sub> E <sup>II</sup> O <sub>2</sub>	E <sup>H</sup> E <sub>2</sub> HO <sub>2</sub>	E <sup>VI</sup> HO <sub>6</sub>
H=4	Li=7	Gl=9	B=11	C=12	N=14	O=16	F=19	.....
Ne=20	Na=23	Mg=24.3	Al=27	Si=28.3	P=31	S=32	Cl=35.5	.....
A=30.9	K=39	Ca=40	Sc=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56 Co=59 Ni=58.7
.....	Cu=63.6	Zn=65.4	Ga=70	Ge=72.5	As=75	Se=79.2	Br=80	.....
Kr=83	Rb=85.4	Sr=87.6	Yt=89	Zr=90.6	Cb=93	Mo=96	.....	Ru=101.7 Rh=103 Pd=106.7
.....	Ag=108	Cd=112.4	In=115	Su=119	Sb=120	Te=127.5	I=127	.....
Xe=130	Cs=133	Ba=137.4	La=139	Ca, etc.* 140-176	Ta=181.5	W=184	.....	Os=191 Ir=193 Pt=195
.....	Au=197	Hg=201	Tl=204	Pb=207	Bi=208	.....	.....	.....
Nt=222.4	.....	Ra=226	.....	Th=232.4	.....	U=238.2	.....	.....

In this table atomic weights are given in round numbers.

\* Pr 140.6, Nd 144.2, Sa 160.4, Eu 162, Gd 157.3, Tb 159.2, Dy 163.5, Ho 165.5, Er 167.7, Tm 168.5, Yb 173.5, Lu 175.